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CONTENTS

SECTION A

PAGE

First Annual Meeting of the Indian Academy of Sciences.—Presidential Address. By C. V. RAMAN, KT., F.R.S., N.L. 1

Unitary Theory of Field and Matter. I. Classical Treatment. Charged Particle with Magnetic Rest-Moment. By MAX BORN 8

The Raman Spectra of Ortho-Phosphoric Acid and Some Phosphates. By C. S. VENKATESWARAN 25

The Occurrence of Furan Derivatives in Volatile Oils—III. β-Clausenan and γ-Clausenan. By B. SANJIVA RAO and K. S. SUBRAMANIAM .. 31

Brucine Sulphate as an Internal Indicator in Titrations with Standard Dichromate Solution. By D. S. NARAYANAMURTHI and T. R. SESHADRI 38

Optic Moments of Organic Molecules in Relation to Crystalline and Magnetic Birefringence. By M. RAMANADHAM 43

Vinogradow's Solution of Waring's Problem (II). By I. CHOWLA .. 51

The Raman Spectra of Some Organic Liquids under High Dispersion and Resolving Power. (Benzene, Toluene, Phenol, Chlorobenzene, Pyridine and Cyclohexane.) By R. ANANTHAKRISHNAN .. 52

The Diffraction of Light by High Frequency Sound Waves: Part III. Doppler Effect and Coherence Phenomena. By C. V. RAMAN and N. S. NAGENDRA NATH 75

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FIRST ANNUAL MEETING OF THE INDIAN ACADEMY OF SCIENCES.

(Held at Bombay on 18th December 1935.)

PRESIDENTIAL ADDRESS.

By Sir C. V. Raman, Kt., F.R.S., N.L.

The Indian Academy of Sciences was registered at Bangalore on the 24th of April 1934, and was formally inaugurated at a public meeting held at the Indian Institute of Science on the 31st July 1934, by Amin-ul-Mulk Sir Mirza M. Ismail, Dewan of Mysore. In the ordinary course of events, the Annual Meeting should have been held in July last. But for various reasons it was felt desirable to postpone it till the cold weather so that it would be possible for the Meeting to be conveniently held at some centre outside Bangalore where our Fellows could assemble. There is a peculiar appropriateness in that the Academy which was inaugurated at Bangalore should hold its first annual meeting at Bombay. It is known to all of you that if Bangalore to-day occupies a significant position in the world of science, it is to no small extent due to the far-sighted generosity of a great and enterprising citizen of Bombay, the late Mr. Jamsetjee Nusserwanjee Tata. At a time when the Universities of India were few in number and were purely examining bodies, Mr. Tata conceived the idea of creating an Imperial Teaching and Research University for the whole of India which would have aims and ideals approximating to those of such ancient foundations of learning as Oxford and Cambridge. In Mr. Harris's life of Tata, we have an authoritative account of the early history of Mr. Tata's scheme. We read that the two reasons which finally lead to Bangalore being the recipient of his princely benefaction to the cause of learning were firstly, the agreeable climate of Bangalore which he regarded as particularly suitable for a centre of advanced teaching and research, and secondly, the generous offer of the Maharaja of Mysore of half a square mile of land, five lakhs of rupees as a capital grant and an annual subsidy of one lakh of rupees towards the establishment of the Institute at Bangalore. Forty years ago, in this way was forged an intellectual link between Bangalore and Bombay which is now indissoluble and which has had and will, I believe, continue to have a far-reaching influence on the progress of science in India.

The idea of establishing an All-India Academy of Sciences was first clearly put forth in an editorial article in the Journal "Current Science"

published from Bangalore in May 1933. After a period of discussion and consultation with scientific men all over India, the decision to inaugurate the Academy with its provisional headquarters at Bangalore was finally taken in April 1934. I shall, in the course of this address, refer more in detail to the progress which has since been achieved by the Academy and which has amply justified that decision. But even at this early stage, it is appropriate to mention the large part which our friends in Bombay have played in achieving that progress. At the present time, no fewer than thirty-eight of our Fellows are resident in the Bombay Presidency. The election of such a large number to the distinction of the fellowship has been a natural consequence of the remarkable development in recent years of scientific research activities in the Bombay Presidency. I shall have more to say about this later in my address, and it will be sufficient to remark now that the published Proceedings of the Academy bear ample witness to the scientific energy of Dr. T. S. Wheeler and his colleagues at the Royal Institute of Science and to the deep interest taken in the progress of the Academy by the officers of the Meteorological Department at Poona, and the schools of scientific research which have developed at Poona and other parts of the Bombay Presidency. For all these reasons, it is very appropriate that we meet to-day at Bombay. I hope that this gathering will be the first of a series to be held year after year at various centres of scientific research in India. It is desirable that the annual meetings of the Academy should serve to bring together its Fellows from various parts of India at least once a year and thus to strengthen the feeling of scientific comradeship that unites them. Science like other products of human activity, stands to gain immensely from the personal contacts of leading workers. It is earnestly to be hoped that our present meeting will furnish opportunities for such contacts and thus serve to promote the cause of the advancement of science in our great country.

Before I pass to review the work and progress of the Academy since its foundation, I must express the gratitude of the Council to Your Excellency in having consented to grace the occasion to-day and encourage us by your presence here. I must also express the gratitude of the Council to the Fellows of the Academy in Bombay headed by Dr. Wheeler our Vice-President, and to the Reception Committee presided over by you Mr. Vice-Chancellor, who have been at immense pains to organise this our first Annual Meeting on a scale worthy of the occasion.

When the Academy was inaugurated, it commenced its activities with 65 Fellows. The Council obtained permission from the General Body of Fellows to elect fresh Fellows up to a maximum of 200 and also Honorary

Fellows up to a maximum of 30 from amongst the most distinguished scientists of the world. This permission has been acted upon and we have to-day 173 Fellows in India and 30 Honorary Fellows. Our Honorary Fellows include some of the most active and influential scientific men in Europe and America, whose sympathy and co-operation will, I am sure, be of the greatest benefit to the Academy.

The British list of Honorary Fellows includes Lord Rutherford, Sir William Bragg, Sir F. Gowland Hopkins, Sir John Russell, Prof. O. W. Richardson, Prof. Robert Robinson, Prof. A. V. Hill, Prof. P. A. M. Dirac, Prof. A. C. Seward and Prof. G. H. Hardy. The American list includes Prof. R. A. Millikan, Prof. A. H. Compton, Prof. N. L. Bowen, Prof. Harvey Cushing, Prof. D. D. Van Slyke and Prof. G. N. Lewis. The German list includes Prof. A. Sommerfeld, Prof. W. Heisenberg, Prof. Hans Fischer, Prof. H. Wieland and Prof. F. Paschen. From France we have Prof. A. Cotton and Madame Irene Curie-Joliot. From Sweden we have Prof. K. M. G. Siegbahn and Prof. Th. Svedberg. From Denmark and Holland we have respectively Prof. Niels Bohr and Prof. P. Zeeman. From Italy we have Prof. E. Fermi and Prof. S. Belfanti and from Russia Prof. I. P. Pavlov.

It is noteworthy that the list of 30 includes one woman scientist, Madame Irene Curie-Joliot. It must have given our Fellows great pleasure to read the recent announcement of the award of the Nobel Prize in Chemistry to this lady and her husband jointly.

Our list of Fellows in India is representative of every important branch of science. Physics and Meteorology are represented by 34 Fellows, Mathematics and Astronomy by 18, Chemistry by 40, Zoology and Anthropology by 17, Agriculture, Forestry and Botany by 35, Medicine by 15 and Geology by 8. We have only 6 Engineering Fellows but they include some very distinguished names including some very familiar in Bombay, *viz.*, Sir M. Visvesvaraya and Dewan Bahadur N. N. Iyengar. Our list of Fellows is also representative of all parts of India. Bombay heads the list with 38 Fellows, closely followed by the Madras Presidency by 35 and Mysore State by 33. Other provinces are also well represented. We have 21 Fellows in the United Provinces ; 13 from the Punjab, 11 from Bengal, 8 from the Central Provinces ; Bihar and Orissa, Hyderabad, Travancore and Burma are also represented in our list.

The scientific activities of the Academy may be considered under the three heads :—

Meetings for discussion of research papers.
Symposia on special subjects.
Publication of the Proceedings.

I shall consider the last first because in a country like India separated by great distances, by far the most important service that can be rendered to science by the Academy is the regular issue of a scientific journal of high standing in which scientific papers of its Fellows can find prompt publication. I think it will be generally agreed that the Academy has achieved very gratifying success in this direction. Ever since the formal inauguration of the Academy, the Proceedings have appeared month after month with unbroken regularity on the due date. A very great amount of material has reached the Academy from many quarters. The examination of this material and the selection of suitable papers has naturally been a formidable task. That it has so far been accomplished without any signs of breakdown is largely due to the co-operation which the Academy has been so fortunate to secure. A special word of praise is due to the Superintendent of the Bangalore Press who has maintained a high standard of printing both as regards accuracy and technical finish and has enabled the Journal to appear with unfailing punctuality. To the numerous Fellows who have acted as referees for papers often at great cost of time and trouble, the Council are deeply indebted. A heavy burden has also fallen on the Secretaries and on the Manager of the office which they have discharged with conspicuous devotion and success. I believe our Fellows have by this time learnt to look forward to the appearance of the Proceedings on the first of every month and to peruse its contents with eagerness and satisfaction. The volume of published material has grown so rapidly that commencing from July 1935 it was found necessary to separate the Proceedings into two parts, A, Physical and Mathematical Series, and B, Biological Series respectively. The two numbers of the Journal appearing in each month have each contained roughly 100 pages of printed matter together with a very substantial number of illustrated plates. In view of the volume of published matter, the Council have decided in future to issue two volumes instead of one per annum for each of the two sections of the Proceedings.

I will next refer to the Symposia organised by the Academy. There was one in August 1934 on Molecular Spectra which was attended by 50 Fellows from all over India. The shorter papers submitted for this symposium have all been published in the Proceedings. A very valuable and detailed report by Prof. R. Samuel of the Aligarh University has already been printed and circulated to leading specialists on the subject. A detailed report by Mr. N. S. Nagendra Nath on the subject of Dynamics of Molecular Vibrations is also to be printed and issued shortly together with Dr. Samuel's Report as a special publication. In October 1935,

a symposium on Disease Resistance in Plants was held at Coimbatore. This was largely attended and was a successful gathering, mainly as the result of the efforts of our Coimbatore friends who worked hard to organise the function. At the present meeting in Bombay, a symposium on Colloid Science has also been arranged.

An important part of the regular work of the Academy is the holding of scientific meetings at which papers presented to it are read and discussed. While such meetings are usually held at Bangalore, the Council have also encouraged the idea of meetings being held at other centres for the reading of papers on the occasion of special gatherings such as Symposia and the annual meetings.

A matter of great concern to the Academy is the question of providing money for these activities, especially for the cost of publication of the Proceedings which is very heavy. That it has been possible at all to carry on the work of the Academy without a complete financial breakdown is largely due to the generosity of the external authorities who have come forward to help us. Chief amongst these, I should mention the Government of His Highness the Maharaja of Mysore who have sanctioned a grant of Rs. 3,000 per annum for a period of five years. His Highness the Ruler of Bhopal has been pleased to sanction an annual recurring grant of Rs. 500, and the Government of His Highness the Maharaja of Cochin have also sanctioned an annual recurring grant of Rs. 250. The Imperial Council of Agricultural Research have sanctioned a grant of Rs. 500 per annum for 3 years. The latest benefaction to the Academy is from the Government of His Highness the Maharaja of Travancore of Rs. 1,000 for this year. The Council of the Indian Institute of Science sanctioned a grant of Rs. 2,000 for the current year. The University of Nagpur have given us Rs. 100 and one of our Fellows, Mr. T. W. Barnard, has made a special contribution of Rs. 50.

It must be obvious that the publication of a scientific journal rather, of two scientific journals appearing month after month, is a very expensive proposition. Unless we have an assured income of at least Rs. 25,000 per annum, it will not be possible to carry on this work in a satisfactory manner. Only about one-third of this sum can be found from the regular subscriptions of our Fellows. In these days, the building up of a subscription list for a new scientific periodical is a slow and difficult business. It is here, however, that great assistance can be rendered to us by the educated public in India. If every college, every scientific institution and every department of the local Governments subscribed, as it should, for one copy of the Proceedings of the Academy, our financial problem would be greatly eased. I earnestly appeal to all the other Governments and Universities in India to

come to our aid. Even a modest annual contribution from each of them would aggregate to a total sum which would enable the Academy to go forward in its great task without fear of financial breakdown.

I think it would be not inopportune to consider at this stage the nature of the services which the Academy can render to science in India. We live in an era of scientific progress and it is a very gratifying feature that India is beginning to pull its weight in this respect. Modern scientific progress shows side by side two apparently contradictory features. On the one hand, we have an enormous accumulation of raw scientific material, the significance of which, in many cases, is hardly apparent except to specialists in very limited fields of investigation. On the other hand, we have a great process of scientific synthesis going on tending towards the simplification and unification of the fundamental principles of natural knowledge in all its ramifications. It should never be overlooked that science is in reality a great impartible estate and that the boundaries drawn across it to divide it into restricted fields are in essence artificial. I think the history of science has shown over and over again that it is only by boldly cutting across these artificial boundaries that progress of real significance can be achieved. It is precisely this feature that lends importance to the activities of such an Academy as ours where men of science of widely different scientific interests come together in a common endeavour and seek to understand each other's points of view. While specialisation is necessary, an excessively narrow outlook defeats the primary purpose of science which is to advance our essential comprehension of nature as a whole. It is, therefore, one of the most important functions of our Academy to promote co-operation between men who profess knowledge of different branches of science. This is effected in various ways. In the Proceedings of the Academy the Fellows and indeed all scientific men have an opportunity of obtaining at least a general idea of what is being done in India in fields of knowledge other than their own speciality. In the scientific meetings of the Academy and especially in the Symposia, they have a valuable opportunity of discussing problems of common interest from different points of view.

I will also say a word about the Academy in relation to the nation at large. It is inevitable that the Academy, consisting as it does of the most active workers in the country who are representatives of the different parts of India and of different branches of science, will soon come to be regarded as the most authoritative body to speak in the name of India on all matters touching the progress of science. The potentialities of such an Academy in the way of national service are almost unlimited. What it can actually

achieve depends on the measure of support and recognition that it receives from the Governments of India and from the general public. I do not think that any calls for service from responsible quarters will find us unwilling or unprepared.

According to the Memorandum of Association, the headquarters of the Academy has been fixed at Bangalore for a period of three years in the first instance. I have no doubt it is the general feeling of all our Fellows that this location has fully justified itself. In this connection, I should mention the generous personal gift by His Highness the Maharaja of Mysore of ten acres of land in the vicinity of the Indian Institute of Science as a permanent location for the Academy. The location selected is a historic spot close to one of the four towers set up by Kempe Gowda, a former Hindu ruler, as a limit for the extension of his city. A relief map shows this site to be the highest spot in Bangalore. Indeed, standing on it at ground-level we see a magnificent panorama stretching out towards the horizon in all directions with Nandidroog in the blue distance towards the north, Sankey's Reservoir and the City of Bangalore to the south, the Palace Gardens to the east and the Indian Institute of Science to the west with the Sivaganga hills looming in the distance. Such a spot is indeed a worthy site for the location of an Academy of Sciences intended to play a great part in the intellectual life of the nation. Such a site also demands a noble edifice which would catch the eye and strike the imagination of both the present and future generations. Has not Bombay some far-sighted and philanthropic donor who would come forward to build an Academy of Sciences for all India and thus immortalize himself and find a place in the memory of India side by side with Jamsetji Tata. The permanent location at Bangalore of an Academy of Sciences would indeed be a fitting completion of Tata's great work. The Academy would serve as a link between the Institute and the outer world of science, each strengthening the other and helping it to reach the full fruition of its aims.

UNITARY THEORY OF FIELD AND MATTER.

I. Classical Treatment. Charged Particle with Magnetic Rest-Moment.

By Max Born.

(*From the Department of Physics, Indian Institute of Science, Bangalore.*)

Received December 3, 1935.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction.

The principal problem of a unitary theory of field and matter is the derivation of the equations of motion of a singularity representing a particle. Several attempts have been made[1] in this direction but none is quite satisfactory. I shall give here a new derivation of the equations of motion of a spinning particle on the basis of the classical treatment of the field equations. This derivation is simple and absolutely rigorous under the suppositions which have to be made so as to give the problem a definite meaning. The chief assumption can be expressed in the usual language of Maxwell's theory in this way : the external field must be constant over the "diameter" of the particle. The unitary field theory does not distinguish between external and internal field ; the corresponding supposition is : the (total) field approaches a constant field at a great distance from the singularity. We shall start from a variation principle representing both the motion of the field and of the singularity. Correspondingly it consists of two parts, a space-time integral and a pure time integral. But we shall write the latter also as space-time integral making use of Dirac's δ-function. In this way a great clearness about the physical interpretation of the equations is reached ; but the mathematical laws can be easily expressed without symbolic functions and this will be done throughout.

This method leads in the most natural way to the introduction of the spin in the classical theory. Kramers[2] has first shown that a classical spin theory is possible, indeed, and that the quantization of it leads to Dirac's wave equation. The spinning particle is considered by Kramers as a mass point connected with an angular momentum the motion of which is

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[1] M. Born and L. Infeld, *Proc. Roy. Soc.*, 1934, **A 144,** 425; E. Feenberg, *Phys. Rev.*, 1935, **47,** 148; T. Frenkel, *Proc. Roy. Soc.*, 1934, **A 416,** 930.

[2] H. A. Kramers, *Physica*, 1934, **1,** 825; Zeeman, *Verhandelingen*, 1935, p. 403.

described by relativistically invariant formulæ. We show how Kramers' formulæ can be derived from the unitary field theory.

The problem of quantization shall be treated later.

1. *Variation principle and field equations.*[3]

The Lagrangian $L(f_{kl})$ of the field is supposed to be invariant for Lorentz transformation; but we do not assume a special function and rely only on the fact proved in previous publications that there exists such a function for which the energy and momentum of a point charge are finite.

To this Lagrangian of the field we add a Lagrangian of the singularity which we suppose to have the form $l(\phi_k, f_{kl})\delta$, where δ is a symbolic function of the type introduced by Dirac. We assume that in the coordinate system where the singularity is at rest, $\delta(x, y, z) = 0$ at every point except in the singularity x_0, y_0, z_0, where δ is infinite in such a way that

$$\int \delta dv = 1, \qquad dv = dxdydz.$$

The assumption that l depends explicitly on the potentials ϕ_k does not lead to any difficulties as in the theory of Mie.[4] He introduced the ϕ_k in the Lagrangian of the field: $L(\phi_k, f_{kl})$; this leads to contradictions to the fact that the absolute value of the potential in free space has no physical meaning. As the absolute value of the potential in the singularity has a definite meaning, the introduction of the ϕ_k in the Lagrangian of the singularity is permitted.

The variation principle governing field and matter is

$$(1,\ 1) \qquad \int \{L(f_{kl}) + l(\phi_k, f_{kl})\delta\}\, dv\, dt = \text{Extremum}.$$

We define the second kind of field components in the usual way by

$$(1,\ 2) \qquad p^{kl} = \frac{\partial L}{\partial f_{kl}};$$

further we put

$$(1,\ 3) \qquad \rho^k = \frac{\partial l}{\partial \phi_k}, \qquad m^{kl} = \frac{\partial l}{\partial f_{kl}}.$$

As the f_{kl} are connected with the potentials ϕ_k by

$$(1,\ 4) \qquad f_{kl} = \frac{\partial \phi_k}{\partial x^l} - \frac{\partial \phi_l}{\partial x^k},$$

one has the identities

$$(1,\ 5) \qquad \frac{\partial f^{*kl}}{\partial x^l} = 0, \qquad \text{or} \quad \frac{\partial f_{kl}}{\partial x^m} + \frac{\partial f_{lm}}{\partial x^k} + \frac{\partial f_{mk}}{\partial x^l} = 0,$$

---

[3] The notations are those used in the previous papers of Born and Infeld, cited above.

[4] G. Mie, *Ann. d. Phys.*, **37**, p. 511; **39**, p. 1; **40**, p. 1.

where f^{*kl} is the dual tensor to f_{kl}; (1, 5) is the first set of field equations. The second set are the Eulerian equations of the variation principle:

$$\frac{\partial p^{kl}}{\partial x^l} = \rho^k \delta - \frac{\partial m^{kl}\delta}{\partial x^l}. \tag{1, 6}$$

From this follows the continuity equation

$$\frac{\partial \rho^k \delta}{\partial x^k} = 0. \tag{1, 7}$$

We introduce now the space-vector notation[5] (with $c = 1$):

$$\left\{\begin{aligned} (\phi^1, \phi^2, \phi^3, \phi^4) &= (\vec{A}, \phi), \\ (f_{23}, f_{31}, f_{12}) &= \vec{B}, \ (f_{14}, f_{24}, f_{34}) = \vec{E}, \\ (p_{23}, p_{31}, p_{12}) &= \vec{H}, \ (p_{14}, p_{24}, p_{34}) = \vec{D}, \\ (\rho^1, \rho^2, \rho^3, \rho^4) &= (e\vec{v}, e), \\ (m_{23}, m_{31}, m_{12}) &= \vec{m}, \ (m_{14}, m_{24}, m_{34}) = \vec{p}, \end{aligned}\right. \tag{1, 8}$$

Then the field equations (1, 5), (1, 6) are

$$\left\{\begin{aligned} \text{rot } \vec{H} - \dot{\vec{D}} &= \delta(e\vec{v} + \dot{\vec{p}}) - \text{rot } (\vec{m}\delta), \\ \text{div } \vec{D} &= \delta e - \text{div } (\vec{p}\delta), \\ \text{rot } \vec{E} + \dot{\vec{B}} &= 0, \\ \text{div } \vec{B} &= 0, \end{aligned}\right. \tag{1, 9}$$

and the equation of continuity (1, 7)

$$\frac{\partial e\delta}{\partial t} + \text{div } (e\vec{v}\,\delta) = 0. \tag{1, 10}$$

The vectors $\vec{p}, \vec{m}$ have obviously to be interpreted as an *electric and magnetic moment*, connected with the singularity.

We assume that in the coordinate system, where the particle is at rest, there is only a magnetic moment (spin) $\vec{m}$.

Then

$$\vec{p} = -(\vec{v} \times \vec{m}). \tag{1, 11}$$

The invariance of the variation principle for Lorentz transformation implies the two identities

---

[5] Pulling up and down of the indices 1, 2, 3 changes the sign; that of the index 4 does not. For instance:

$$(\rho_1, \rho_2, \rho_3, \rho_4) = (-e\vec{v}, e).$$

$$(1,\ 12)\qquad \begin{cases} \vec{E} \times \vec{H} = \vec{D} \times \vec{B}, \\ \vec{E} \times \vec{D} = -\vec{H} \times \vec{B}, \end{cases}$$

which express that L depends only on the invariants

$$\vec{B}^2 - \vec{E}^2, \quad \vec{E} \cdot \vec{B}.$$

For the line integral we have to suppose invariance as well ; this leads to the identities

$$(1,\ 13)\qquad \begin{cases} (\vec{E} \times \vec{m})_0 = (\vec{p} \times \vec{B})_0, \\ (\vec{E} \times \vec{p})_0 = -(\vec{m} \times \vec{B})_0, \end{cases}$$

where the index 0 indicates that the co-ordinates of the singularity have to be substituted.

In the rest-system, where $\vec{v} = 0$, $\vec{p} = 0$, one has

$$(1,\ 14)\qquad \left.\begin{array}{l} (\vec{E} \times \vec{m})_0 = 0, \quad (\vec{p} \times \vec{B})_0 = 0, \\ (\vec{E} \times \vec{p})_0 = 0, \quad (\vec{m} \times \vec{B})_0 = 0 \end{array}\right\} v = 0.$$

If any quantity F vanishes at the singularity one has

$$\left[\frac{dF}{dt}\right]_0 = \left[\vec{v} \cdot \operatorname{grad} F + \frac{\partial F}{\partial t}\right]_0 = 0,$$

therefore in the rest system :

$$(1,\ 15)\qquad \left(\frac{\partial F}{\partial t}\right)_0 = 0, \text{ for } v = 0, \text{ if } \Big(F(v)\Big)_0 = 0.$$

Applying this to (1, 13) we get :

$$(1,\ 16)\qquad \begin{cases} \left[\frac{\partial}{\partial t}(\vec{E} \times \vec{m}) - \frac{\partial}{\partial t}(\vec{p} \times \vec{B})\right]_0 = 0, \\ \left[\frac{\partial}{\partial t}(\vec{E} \times \vec{p}) + \frac{\partial}{\partial t}(\vec{m} \times \vec{B})\right]_0 = 0. \end{cases}$$

2. *Boundary conditions at the singularities.*

The equations (1, 9) are equivalent to the postulate, that the corresponding homogeneous equations

$$(2,\ 1)\qquad \begin{cases} \operatorname{rot} \vec{H} - \dot{\vec{D}} = 0, \quad \operatorname{rot} \vec{E} + \dot{\vec{B}} = 0, \\ \operatorname{div} \vec{D} = 0, \qquad\qquad \operatorname{div} \vec{B} = 0 \end{cases}$$

hold at any point except at the singularity where certain boundary conditions have to be fulfilled. These are found by integrating the differential equations (1, 9) directly, and after multiplying them by x, y, z, over a small

sphere. The essence of the unitary theory of matter and field consists in the assumption that all volume integrals of the types

$$\int_0 \mathrm{D}_x \, dv, \quad \int_0 \mathrm{D}_x y \, dv, \quad \int_0 \dot{\mathrm{D}}_x \, dv, \quad \int_0 \dot{\mathrm{D}}_x y \, dv, \cdots\cdots$$

vanish if the radius of the sphere is contracting to zero, even if the sphere contains a singularity. But the volume integrals of space derivatives (rot, div) can be transformed into surface integrals, which tend to finite values. In the rest-system of the singularity we get easily from (1,9), (1, 10) :

$$(2,\ 2) \qquad \dot{e} = 0,$$

$$(2,\ 3) \quad \begin{cases} \int_0 (\vec{n} \times \vec{\mathrm{H}})\, d\sigma = 0, & \int_0 \vec{n} \cdot \vec{\mathrm{D}}\, d\sigma = e, \\ \int_0 (\vec{n} \times \vec{\mathrm{E}}) d\sigma = 0, & \int_0 \vec{n} \cdot \vec{\mathrm{B}}\, d\sigma = 0\,; \end{cases}$$

$$(2,\ 4) \quad \begin{cases} \int_0 x\, (\vec{n} \times \vec{\mathrm{H}})_x \, d\sigma = 0, \cdots\cdots\cdots \\ \int_0 y\, (\vec{n} \times \vec{\mathrm{H}})_x \, d\sigma = m_z, \cdots\cdots\cdots \\ \int_0 z\, (\vec{n} \times \vec{\mathrm{H}})_x \, d\sigma = -\, m_y, \cdots\cdots \end{cases}$$

$$(2,\ 5) \qquad \int_0 \vec{r}\, (\vec{n} \cdot \vec{\mathrm{D}})\, d\sigma = e\, \vec{r}_0,$$

$$(2,\ 6) \quad \begin{cases} \int_0 x\, (\vec{n} \times \vec{\mathrm{E}})_x \, d\sigma = 0, \cdots\cdots\cdots \\ \int_0 y\, (\vec{n} \times \vec{\mathrm{E}})_x \, d\sigma = 0, \cdots\cdots\cdots \\ \int_0 z\, (\vec{n} \times \vec{\mathrm{E}})_x \, d\sigma = 0, \cdots\cdots\cdots \end{cases}$$

$$(2,\ 7) \qquad \int_0 \vec{r}\, (\vec{n} \cdot \vec{\mathrm{B}})\, d\sigma = 0.$$

Here $\vec{n}$ is the unit vector normal to the surface element $d\sigma$ of the sphere surrounding the singularity.

3. Dynamical boundary conditions at the singularity.

Tc make full use of the variation principle (1, 1) we have not only to vary the field for a given motion of the singularity, but also to vary this motion, *i.e.*, the functions, $\vec{r}_0(t)$, $\vec{m}(t)$ for a given field. This variation influences only the Lagrangian l of the singularity. Now we can assume that l has the form

$$(3,\ 1)\quad l = \rho^k \phi_k + \tfrac{1}{2} m^{kl} f_{kl} = e(\phi - \vec{v}\cdot\vec{A}) + \vec{m}\cdot\vec{B} - \vec{p}\cdot\vec{E},$$

since this gives the same field equation (1, 9).

Here ϕ, $\vec{A}$, $\vec{B}$, $\vec{E}$ are to be considered as functions of $\vec{r}_0(t)$, whereas $\vec{v} = \dot{\vec{r}}_0(t)$, $\vec{p} = \vec{m}(t) \times \dot{\vec{r}}_0(t)$.

If ϕ, $\vec{A}$, $\vec{B}$, $\vec{E}$ were continuous functions of their arguments, one could apply directly the formal rules of the calculus of variations on the integral $\int l dt$. But in fact these functions are just supposed to have a singular point at $\vec{r}_0$, and the assumption, that the spatial derivatives exist, is not justified. Therefore we have to make the variation in a more elaborate way.

We replace $e\delta$, $e\vec{v}\delta$ by a little more general δ-functions, ρ, $\rho\vec{v}$; these are first considered as continuous distributions of density and current around the world line which has to become the representation of the moving singularity. We introduce instead of x, y, z, t, the parameters ξ, η, ζ, τ, where τ is the proper time for each world line in the continuous current ρ, $\rho\vec{v}$, given by a special set of values of the parameters ξ, η, ζ. Then the variation principle can be written

$$(3,\ 2)\quad \int d\tau \iiint d\xi d\eta d\zeta \left\{ \dot{t}\,(\rho_0\phi + \vec{m}\cdot\vec{B}) - \dot{\vec{r}}_0\left(\rho_0\vec{A} - (\vec{m}\times\vec{E})\right)\right\} = \text{Extr.},$$

where $\rho_0(\xi, \eta, \zeta)$ is the rest density, and $\vec{r}_0(\xi, \eta, \zeta, \tau)$, $t_0(\xi, \eta, \zeta, \tau)$ are the unknown functions; the point indicates the derivative with respect to τ.

We assume that the functions ϕ, $\vec{A}$, $\vec{B}$, $\vec{E}$ are continuously depending on their arguments x_0, y_0, z_0, t_0, and that their singularities appear only when the continuous current is contracted to a world line. We shall show that these singularities have no influence on the differential equation of the extremal curve.

We have to add the condition expressing τ being the proper time:

$$(3,\ 3)\quad \dot{t}_0^2 - \dot{x}_0^2 - \dot{y}_0^2 - \dot{z}_0^2 = 1.$$

The variation principle (3, 2) is a generalisation of the well-known principle giving Lorentz equations of motion:

$$\int d\tau \iiint d\xi d\eta d\zeta \cdot \rho_0 (\dot{t}_0 \phi - \dot{\vec{r}}_0 \cdot \vec{A}) = \text{Extr.},$$

and can be treated in exactly the same way. We take account of the subsidiary condition (3, 3) by a Lagrangian multiplier $\mu(\xi, \eta, \zeta, \tau)$; then we get

$$(3,\ 4)\quad \begin{cases} \iiint d\xi d\eta d\zeta \left(\dfrac{d\mu\, \dot{\vec{r}}_0}{d\tau} - \vec{K} \right) = 0, \\ \iiint d\xi d\eta d\zeta \left(\dfrac{d\mu \dot{t}_0}{d\tau} - \kappa \right) = 0, \end{cases}$$

where

$$(3,\ 5)\quad \begin{cases} \vec{K} = \dot{t}_0 \left(\rho_0 \vec{E} - \text{grad}\, (\vec{m} \cdot \vec{B}) \right) + \rho_0 \left(\dot{\vec{r}}_0 \times \vec{B} \right) + \dfrac{d}{dt} (\vec{m} \times \vec{E}) \\ \qquad\qquad - \left[\dot{\vec{r}}_0 \times \text{rot}\, (\vec{m} \times \vec{E}) \right], \\ \kappa = (\rho_0 \dot{\vec{r}}_0 \cdot \vec{E}) + \dot{\vec{r}}_0 \left[\dfrac{d}{dt} (\vec{m} \times \vec{E}) - \text{grad}\, (\vec{m} \cdot \vec{B}) \right]. \end{cases}$$

Now we can make the limiting process of contracting the current to a world line. Since the space ξ, η, ζ is normal to this line, we can transform it to rest; then $\dot{\vec{r}}_0 = 0$, $\dot{t}_0 = 1$, and we get

$$(3,\ 6)\quad \left\{ \begin{array}{l} \left\{ \dfrac{d\mu\, \vec{v}}{dt} - e \vec{E} + \text{grad}\, (\vec{m} \cdot \vec{B}) - \dfrac{d}{dt} (\vec{m} \times \vec{E}) \right\}_0 = 0, \\ \left\{ \dfrac{d\mu}{dt} \right\}_0 = 0 \end{array} \right\} v = 0.$$

Besides these equations we get another one by varying $\vec{m}$ in (3, 2); this gives obviously

$$(3,\ 7)\qquad \left(\vec{B} - [\vec{v} \times \vec{E}] \right)_0 = 0,$$

and in the rest-system:

$$(3,\ 8)\qquad \vec{B}_0 = 0 \qquad \text{for } \vec{v} = 0.$$

The multiplier μ plays the rôle of a (constant) mass, concentrated in a point. The assumption of a point mass is consistent with the mathematical formalism, but in contradiction to the idea of the unitary field theory.

We take therefore

$$(3,\ 9)\qquad \mu = 0$$

and have the *dynamical boundary conditions :*

$$(3,\ 10)\quad \vec{K}^{\circ} = \left[e\vec{E} - \operatorname{grad}(\vec{m}\cdot\vec{B}) + \frac{d}{dt}(\vec{m}\times\vec{E})\right]_0 = 0.$$

From (3, 7) and (1, 11) it follows that

$$(3,\ 11)\quad (\vec{m}\cdot\vec{B} - \vec{p}\cdot\vec{E})_0 = 0.$$

Corresponding to the remark at the end of section 1, there is also

$$(3,\ 12)\quad \left[\frac{d}{dt}(\vec{m}\cdot\vec{B})\right]_0 = \left[\frac{d}{dt}(\vec{p}\cdot\vec{E})\right]_0 = 0 \quad \text{for } \vec{v} = 0.$$

4. Conservation laws.

We multiply (1, 5) by $p^{ln} + \delta m^{ln}$ and sum over l, n :

$$\frac{\partial L_k}{\partial x^k} + \frac{\partial}{\partial x^l}(p^{ln}f_{nk}) = f_{nk}\frac{\partial p^{nl}}{\partial x^l} - \delta\left(\tfrac{1}{2}m^{ln}\frac{\partial f_{ln}}{\partial x^k} + m^{ln}\frac{\partial f_{nk}}{\partial x^l}\right).$$

With help of (1, 6) we get :

$$(4,\ 1)\quad \frac{\partial}{\partial x^l}(L\delta_k^l - p^{nl}f_{nk}) = \delta\left(f_{kn}\rho^n - \tfrac{1}{2}m^{ln}\frac{\partial f_{ln}}{\partial x^l}\right) + \frac{\partial}{\partial x^l}(m^{ln}f_{kn}\delta).$$

We define the energy-momentum tensor

$$(4,\ 2)\quad T_k^l = L\delta_k^l - p^{ln}f_{kn},$$

and the corresponding tensor

$$(4,\ 3)\quad t_k^l = \lambda\delta_k^l - m^{ln}f_{kn}$$

where

$$(4,\ 4)\quad \lambda = \tfrac{1}{2}m^{nl}f_{nl}.$$

Then (4, 1) becomes :

$$(4,\ 5)\quad \frac{\partial T_k^l}{\partial x^l} = \delta f_{kn}\rho^n + \tfrac{1}{2}f_{nl}\frac{\partial(m^{nl}\delta)}{\partial x^k} - \frac{\partial(t_k^l\delta)}{\partial x^l}.$$

Now we go over to the space-vector notation :

$$(4,\ 6)\quad (T_k^l) = \begin{Bmatrix} X_x & X_y & X_z & S_x \\ Y_x & Y_y & Y_z & S_y \\ Z_x & Z_y & Z_z & S_z \\ S_x & S_y & S_z & U \end{Bmatrix},$$

where Maxwell's tensions

$$(4,\ 7)\quad \begin{cases} X_x = -H_yB_y - H_zB_z + D_xE_x + L, \ \cdots\cdots\cdots \\ X_y = Y_x = -H_yB_x + D_xE_y = -H_xB_y + D_yE_x, \ \cdots, \end{cases}$$

the Poynting vector

$$(4,\ 8)\quad \vec{S} = \vec{E}\times\vec{H} = \vec{D}\times\vec{B},$$

the energy density

$$(4,\ 9)\quad U = \vec{E}\cdot\vec{D} + L;$$

and correspondingly

$$\lambda = \vec{m}\cdot\vec{B} - \vec{p}\cdot\vec{E})_0, \tag{4, 10}$$

$$t_k^i = \begin{Vmatrix} x_x & x_y & x_z & s_x \\ y_x & y_y & y_z & s_y \\ z_x & z_y & z_z & s_z \\ s_x & s_y & s_z & u \end{Vmatrix} \tag{4, 11}$$

This tensor is symmetric on account of (1, 13) and (3, 11):

$$\begin{cases} x_x = (-p_yE_y - p_zE_z + m_zB_x)_0 = (-m_yB_y - m_zB_z + p_xE_x)_0, \cdots \\ x_y = y_x = (-m_yB_x + p_xE_y)_0 = (-m_xB_y + p_yE_x)_0, \cdots \\ \vec{s} = (\vec{E}\times\vec{m})_0 = -(\vec{B}\times\vec{p})_0, \\ u = (\vec{m}\cdot\vec{B})_0 = (\vec{p}\cdot\vec{E})_0. \end{cases} \tag{4, 12}$$

In consequence of (1, 11) and (3, 8) all these quantities vanish in the rest-system:

$$\left.\begin{cases} \lambda = 0 \\ x_x = 0, \cdots\cdots x_y = y_x = 0, \cdots\cdots \\ \vec{s} = 0 \\ u = 0 \end{cases}\right\} \text{for } \vec{v} = 0. \tag{4, 13}$$

We write now (4, 5) for the rest-system:

$$\begin{cases} \dfrac{\partial S_x}{\partial t} + \operatorname{div}\vec{X} = \delta e E_x + \vec{B}\cdot\dfrac{\partial \vec{m}\delta}{\partial x} - \vec{E}\cdot\dfrac{\partial \vec{p}\delta}{\partial x} - \delta\dot{\vec{s}}_x - \operatorname{div}(\vec{x}\delta), \\ - - - - - - \\ - - - - - - \\ \dfrac{\partial U}{\partial t} + \operatorname{div}\vec{S} = \delta(\vec{B}\cdot\dot{\vec{m}} - \vec{E}\,\dot{\vec{p}}) - \delta\dot{u} - \operatorname{div}(\vec{s}\,\delta). \end{cases} \tag{4, 14}$$

We integrate over a small sphere surrounding the singularity:

$$\int_0 (\vec{X}\cdot\vec{n})\,d\sigma = \left[eE_x - \vec{m}\cdot\frac{\partial\vec{B}}{\partial x} + \frac{d}{dt}(\vec{m}\times\vec{E})_x\right]_0 = K_x{}^0,$$

$$- - - -$$

$$- - - -$$

$$\int_0 (\vec{S}\cdot\vec{n})\,d\sigma = 0;$$

here we have made use of the remark at the end of the last section of putting equal to zero the time derivatives of all quantities which vanish in the rest-system.

Comparing this with (3, 6) we find

$$(4, 15)\qquad \begin{cases} \int\limits_0 (\vec{X}\cdot\vec{n})\, d\sigma = 0, \ \cdots \\ \int\limits_0 (\vec{S}\cdot\vec{n})\, d\sigma = 0. \end{cases}$$

Now we multiply the third equation (4, 14) with y, the second with z, subtract and integrate; then we find in exactly the same way

$$(4, 16)\qquad \int\limits_0 (\vec{N}_x\cdot\vec{n})\, d\sigma = (\vec{r}_0 \times \vec{K}^0)_x = 0,$$

where

$$(4, 17)\qquad \vec{N}_x = (yZ_x - zY_x, \quad yZ_y - zY_y, \quad yZ_z - zY_z), \ \cdots,$$

The operation applied to (4, 14) which leads to (4, 16) must be completed by multiplying the first equation by t, the last by x, and integrating; then it represents a 6-vector (antisymmetrical tensor). But since t is constant with respect to the integration, the term with t vanishes in consequence of (4, 15), and we have

$$\int\limits_0 \left(x\,\frac{\partial U}{\partial t} + x \operatorname{div} \vec{S}\right) dv = x_0(\vec{B}\cdot\dot{\vec{m}} - \vec{E}\cdot\dot{\vec{p}} - \dot{u})_0$$

$$= - x_0(\dot{\vec{m}}\cdot\vec{B} - \dot{\vec{p}}\cdot\vec{E})_0.$$

In the rest-system, according to (3, 12), $\left[\frac{d}{dt}(\vec{m}\cdot\vec{B})\right]_0 = 0$ or, since $\vec{B}_0 = 0$, for $\vec{v} = 0$, $(\dot{\vec{m}}\cdot\vec{B})_0 = 0$, for $\vec{v} = 0$; therefore the right hand term vanishes. We get

$$(4, 18)\qquad \int\limits_0 \vec{r}\,(\vec{S}\cdot\vec{n})\, d\sigma = 0,$$

as the complement of (4, 16) to a 6-vector equation.

We can now replace the equations (4, 14) containing δ-functions by the postulate, that

$$(4, 19)\qquad \begin{cases} \dfrac{\partial \vec{S}_x}{\partial t} + \operatorname{div} \vec{X} = 0, \ \cdots \\ \dfrac{\partial U}{\partial t} + \operatorname{div} \vec{S} = 0 \end{cases}$$

holds for all fields satisfying the dynamical boundary conditions (4, 15) and (4, 18) {(4, 16) being a consequence of (4, 15)}.

5. Equations of motion in a constant field.

We define the *total energy and momentum*

$$(5,\ 1) \qquad \mathrm{E} = \int \mathrm{U} dv, \quad \vec{\mathrm{G}} = \int \vec{\mathrm{S}}\, dv,$$

the *centre of energy* $\vec{q}$

$$(5,\ 2) \qquad \mathrm{E}\,\vec{q} = \int \vec{r}\,\mathrm{U} dv,$$

the *total angular momentum*

$$(5,\ 3) \qquad \vec{\mathrm{M}} = \int (\vec{r} \times \vec{\mathrm{S}})\, dv.$$

We integrate (4, 19) over the whole space, after excluding the singularity by a little sphere; then we do the same after having multiplied the third equation by y, the second by z and subtracting them; at last we do the same after having multiplied the last equation by x. In consequence of the dynamical boundary conditions the integrals over the little sphere vanish, and we get:

$$(5,\ 4) \qquad \begin{cases} \dot{\mathrm{G}}_x + \int\limits_{\infty} (\vec{\mathrm{X}} \cdot \vec{n})\, d\sigma = 0, \ \cdots \\ \dot{\mathrm{E}} + \int\limits_{\infty} (\vec{\mathrm{S}} \cdot \vec{n})\, d\sigma = 0, \end{cases}$$

$$(5,\ 5) \qquad \begin{cases} \dot{\mathrm{M}}_x + \int\limits_{\infty} (\vec{\mathrm{N}}_x \cdot \vec{n})\, d\sigma = 0, \ \cdots \\ \dfrac{d}{dt}(\mathrm{E}\vec{q}) - \vec{\mathrm{G}} + \int \vec{r}\,(\vec{\mathrm{S}} \cdot \vec{n})\, d\sigma = 0. \end{cases}$$

We shall now consider the case where the field in infinity tends to a constant field E^e, B^e (independent of co-ordinates and time). We represent the total field by

$$(5,\ 6) \quad \vec{\mathrm{E}} = \vec{\mathrm{E}}^e + \vec{\mathrm{E}}^i, \quad \vec{\mathrm{B}} = \vec{\mathrm{B}}^e + \vec{\mathrm{B}}^i;$$

then $\vec{\mathrm{E}}^i$ and $\vec{\mathrm{B}}^i$ tend to zero at infinity:

$$(5,\ 7) \quad \lim_{\infty} \vec{\mathrm{E}}^i = 0; \quad \lim_{\infty} \vec{\mathrm{B}}^i = 0.$$

We define the constants

$$(5,\ 8) \quad \vec{\mathrm{D}}^e = -\left(\frac{\partial \mathrm{L}}{\partial \vec{\mathrm{E}}}\right)_{\substack{\vec{\mathrm{E}} = \vec{\mathrm{E}}^e, \\ \vec{\mathrm{B}} = \vec{\mathrm{B}}^e}}, \qquad \vec{\mathrm{H}}^e = \left(\frac{\partial \mathrm{L}}{\partial \vec{\mathrm{B}}}\right)_{\substack{\vec{\mathrm{E}} = \vec{\mathrm{E}}^e, \\ \vec{\mathrm{B}} = \vec{\mathrm{B}}^e}},$$

and split the total field $\vec{D}, \vec{H}$ into $\vec{D}^e, \vec{H}^e$ and a variable part, which may be denoted by $\vec{D}^i, \vec{H}^i$:

$$(5,\ 9)\quad \vec{D} = \vec{D}^e + \vec{D}^i,\quad \vec{H} = \vec{H}^e + \vec{H}^i;$$

then $\vec{D}^i, \vec{H}^i$ depend not only on $\vec{E}^i, \vec{B}^i$, but also on $\vec{E}^e, \vec{B}^e$; but we have in any case

$$(5,\ 10)\quad \lim_{\infty} \vec{D}^i = 0,\quad \lim_{\infty} \vec{B}^i = 0.$$

The field $\vec{E}^i, \vec{B}^i, \vec{D}^i, \vec{H}^i$ satisfies not only Maxwell's equations in the form (2, 1), but also the boundary conditions (2, 2), $\cdots$ (2, 7), since a constant field reduces all the surface integrals to zero.

For the Poynting vector we use first $\vec{S} = \vec{D} \times \vec{B}$; replacing here the vectors $\vec{D}, \vec{B}$ by the sums $\vec{D}^e + \vec{D}^i, \vec{B}^e + \vec{B}^i$, we have

$$\vec{S} = \vec{S}^e + (\vec{D}^e \times \vec{B}^i) + (\vec{D}^i \times \vec{B}^e) + \vec{S}^i$$

where $\vec{S}^i = \vec{D}^i \times \vec{B}^i$ and $\vec{S}^e$ a constant, which can be omitted since it does not contribute to (4, 19). We have therefore

$$(5,\ 11)\quad \vec{G} = \vec{G}^i + (\vec{D}^e \times \int \vec{B}^i\, dv) - (\vec{B}^e \times \int \vec{D}^i\, dv).$$

In the same way we get

$$(5,\ 12)\quad M_x = M_x{}^i + D_x{}^e \int (\vec{r} \cdot \vec{B}^i)\, dv - \vec{D}^e . \int \vec{r}\, B_x{}^i\, dv$$

$$- B_x{}^e \int (\vec{r} \cdot \vec{D}^i)\, dv + \vec{B}^e . \int \vec{r}\, D_x{}^i\, dv, \ \cdots.$$

The energy cannot be split in the same way as it is not a quadratic expression.

We consider now the surface integrals in (5, 4), (5, 5). Here we can develop the integrands with respect to $\vec{E}^i, \vec{B}^i$ or $\vec{D}^i, \vec{H}^i$, as on a very distant surface they are small compared with the external field, however this may be chosen [equations (5, 7), (5, 10)].

The vector $\vec{X}$ with the components X_x, X_y, X_z is given by (4, 7) with help of I_ι; if we introduce instead the energy density U by (4, 9), for which as a function of $\vec{D}, \vec{B}$ one has

$$(5,\ 13)\quad \vec{E} = \frac{\partial U}{\partial \vec{D}},\quad \vec{H} = \frac{\partial U}{\partial \vec{B}},$$

and make use of (4, 7), we have

$$(5,\ 14)\quad \begin{cases} X_x = -H_y B_y - H_z B_z - D_y E_y - D_z E_z + U, \\ X_y = -H_x B_y + E_x D_y, \\ X_z = -H_x B_z + E_x D_z. \end{cases}$$

Introducing here (5, 6), (5, 9) and neglecting the terms of the second order, we get easily

$$(5,\ 15)\quad (\vec{X}\cdot\vec{n}) = (\vec{X}^e\cdot\vec{n}) + H_x{}^e\,(\vec{B}^i\cdot\vec{n}) + E_x{}^e\,(\vec{D}^i\cdot\vec{n}) - [\vec{B}^e\times(\vec{n}\times\vec{H}^i)]_x - [\vec{D}^e\times(\vec{n}\times\vec{E}^i)]_x.$$

For $\vec{S}$ we use the expression $\vec{E}\times\vec{H}$ and get

$$(5,\ 16)\quad (\vec{S}\cdot\vec{n}) = (\vec{S}^e\cdot\vec{n}) - \vec{E}^e\,(\vec{n}\times\vec{H}^i) + \vec{H}^e\,(\vec{n}\times\vec{E}^i).$$

A similar, a little lengthy, calculation leads to

$$(5,\ 17)\quad (\vec{N}_x\cdot\vec{n}) = (\vec{N}_x{}^e\cdot\vec{n}) + \vec{B}^e\cdot\int\vec{r}\,(\vec{n}\times\vec{H}^i)_x\,d\sigma - B_x{}^e\int\vec{r}\cdot(\vec{n}\times\vec{H}^i)\,d\sigma + \vec{D}^e\cdot\int\vec{r}\,(\vec{n}\times\vec{E}^i)_x\,d\sigma - D_x{}^e\int\vec{r}\cdot(\vec{n}\times\vec{E}^i)\,d\sigma - [\vec{H}^e\times\int\vec{r}\,(\vec{n}\cdot\vec{B}^i)\,d\sigma]_x - [\vec{E}^e\times\int\vec{r}\,(\vec{n}\cdot\vec{D}^i)\,d\sigma]_x.$$

Now we integrate Maxwell's equation (2, 1) over the whole space except a little sphere around the singularity; the surface integrals over this sphere are given by (2, 3), $\cdots$ (2, 7), with opposite signs (because of the reversed direction of the outer normal). So we have

$$(5,\ 18)\quad \begin{cases} \int_\infty(\vec{n}\times\vec{H}^i)\,d\sigma = \int\dot{\vec{D}}^i\,dv, \quad \int_\infty(\vec{n}\cdot\vec{D}^i)\,d\sigma = -e \\ \int_\infty(\vec{n}\times\vec{E}^i)\,d\sigma = -\int\dot{\vec{B}}^i\,dv, \quad \int_\infty(\vec{n}\cdot\vec{B}^i)\,d\sigma = 0; \end{cases}$$

$$(5,\ 19)\quad \begin{cases} \int_\infty x\,(\vec{n}\times\vec{H}^i)_x\,d\sigma = \int x\,\dot{D}_x{}^i\,dv, \ \cdots \\ \int_\infty y\,(\vec{n}\times\vec{H}^i)_x\,d\sigma = \int(y\,\dot{D}_x{}^i + H_z{}^i)\,dv - m_z, \ \cdots \\ \int_\infty z\,(\vec{n}\times\vec{H}^i)_x\,d\sigma = \int(z\,\dot{D}_x{}^i - H_y{}^i)\,dv + m_y, \ \cdots \end{cases}$$

$$(5,\ 20)\quad \int_\infty\vec{r}\,(\vec{n}\cdot\vec{D}^i)\,d\sigma = \int\vec{D}^i\,dv - e\,\vec{r}_0,$$

$$(5,\ 21)\quad \begin{cases} \int_{\infty} x\ (\vec{n} \times \vec{E}^i)_x\ d\sigma = -\int x\ \dot{B}_x{}^i\ dv, \cdots \\ \int_{\infty} y\ (\vec{n} \times \vec{E}^i)_x\ d\sigma = -\int (y\ \dot{B}_x{}^i - E_z{}^i)\ dv, \cdots \\ \int_{\infty} z\ (\vec{n} \times \vec{E}^i)_x\ d\sigma = -\int (z\ \dot{B}_x{}^i + E_y{}^i)\ dv, \cdots \end{cases}$$

$$(5,\ 22)\quad \int_{\infty} \vec{r}\ (\vec{n} \cdot \vec{B}^i)\ d\sigma = \int \vec{B}^i\ dv.$$

Introducing this into (5, 15), (5, 16), (5, 17), and integrating we get :

$$(5,\ 23)\quad \int_{\infty} (\vec{X} \cdot \vec{n})\ d\sigma = -eE_x{}^e - \left[\vec{B}^e \times \int \dot{\vec{D}}^i\ dv\right]_x + \left[\vec{D}^e \times \int \dot{\vec{B}}^i\ dv\right]_x,$$

$$(5,\ 24)\quad \int_{\infty} (\vec{S} \cdot \vec{n})\ d\sigma = -\vec{E}^e \cdot \int \dot{\vec{D}}^i\ dv - \vec{H}^e \cdot \int \dot{\vec{B}}^i\ dv,$$

$$(5,\ 25)\quad \int_{\infty} (N_x \cdot \vec{n})\, d\sigma = \vec{B}^e \cdot \int \vec{r}\ \dot{D}_x{}^i\ dv - B_x{}^e \int (\vec{r} \cdot \dot{\vec{D}}^i)\ dv$$

$$- \vec{D}^e \cdot \int \vec{r}\ \dot{B}_x{}^i\ dv + D_x{}^e \int (\vec{r} \cdot \dot{\vec{B}}^i)\ dv$$

$$+ \left(\vec{B}^e \times \int \vec{H}^i\ dv\right)_x - \left(\vec{H}^e \times \int \vec{B}^i\ dv\right)_x$$

$$+ \left(\vec{D}^e \times \int \vec{E}^i\ dv\right)_x - \left(\vec{E}^e \times \int \vec{D}^i\ dv\right)_x$$

$$+ (\vec{m} \times \vec{B}^e)_x - e\ (\vec{r}_0 \times \vec{E}^e)_x.$$

Now from (1, 12) it follows that

$$(\vec{B}^e \times \vec{H}^i) - (\vec{H}^e \times \vec{B}^i) + (\vec{D}^e \times \vec{E}^i) - (\vec{E}^e \times \vec{D}^i) = 0\,;$$

hence (5, 25) reduces to

$$(5,\ 26)\quad \int_{\infty} (N_x \cdot \vec{n})\ d\sigma = \vec{B}^e \cdot \int \vec{r}\ \dot{D}_x{}^i\ dv - B_x{}^e \int (\vec{r} \cdot \dot{\vec{D}}^i)\ dv$$

$$- \vec{D}^e \cdot \int \vec{r}\ \dot{B}_x{}^i\ dv + D_x{}^e \int (\vec{r} \cdot \dot{\vec{B}}^i)\ dv$$

$$+ (\vec{m} \times \vec{B}^e)_x - e\ (\vec{r}_0 \times \vec{E}^e)_x.$$

If we substitute (5, 11), (5, 12) and (5, 23), (5, 24), (5, 26) into (5, 4) and (5, 5) we see that all terms containing volume integrals cancel one another,

and we get:

$$(5,\ 27)\qquad \frac{d\vec{G}^i}{dt} = e\,\vec{E}^e,$$

$$(5,\ 28)\qquad \frac{d\vec{M}^i}{dt} = (\vec{B}^e \times \vec{m}) - (\vec{er}_0 \times \vec{E}^e).$$

If $\vec{M}^i$ is referred to the singularity as origin, then $\vec{r}_0 = 0$, and the second term in the right hand side vanishes.

The energy has to be treated a little differently. We have

$$\frac{dE}{dt} = \frac{d}{dt}\int U dv = \int\left(\frac{\partial U}{\partial \vec{B}}\,\dot{\vec{B}} + \frac{\partial U}{\partial \vec{D}}\,\dot{\vec{D}}\right) dv$$

$$= \int\left(\vec{H}\cdot\dot{\vec{B}} + \vec{E}\cdot\dot{\vec{D}}\right) dv.$$

Introducing here (5, 6) and (5, 9), we get

$$(5,\ 29)\qquad \frac{dE}{dt} = \int\left(\vec{H}^e\cdot\dot{\vec{B}}^i + \vec{E}^e\cdot\dot{\vec{D}}^i + \vec{H}^i\cdot\dot{\vec{B}}^i + \vec{E}^i\cdot\dot{\vec{D}}^i\right) dv.$$

If we now define the internal energy density as the value of the function $U(\vec{B}, \vec{D})$, for the arguments $\vec{B}^i$, $\vec{D}^i$;

$$(5,\ 30)\qquad U^i = U(\vec{B}^i, \vec{D}^i),$$

and the total internal energy as

$$(5,\ 31)\qquad E^i = \int U^i dv,$$

then

$$(5,\ 32)\qquad \frac{dE^i}{dt} = \int(H^i\cdot\dot{\vec{B}}^i + \vec{E}^i\cdot\dot{\vec{D}}^i)\, dv,$$

and (5, 29) becomes

$$(5,\ 33)\qquad \frac{dE}{dt} = \frac{dE^i}{dt} + \vec{H}^e\cdot\int\dot{\vec{B}}^i\, dv + \vec{E}^e\cdot\int\dot{\vec{D}}^e\, dv.$$

Substituting this and (5, 24) into (5, 4), we get

$$(5,\ 34)\qquad \frac{dE^i}{dt} = 0.$$

For the quasi-stationary case we have $\vec{G}^i = E^i\,\vec{v}$; therefore in the rest-system

$$(5,\ 34a)\qquad E_0^i = \text{const.},\qquad \vec{G}_0^i = 0,\qquad \text{for } \vec{v} = 0.$$

In the same way we treat the last equation (5, 5). We find

$$\frac{d}{dt}(\mathrm{E}\,q_x) = \frac{d}{dt}\left(\mathrm{E}^i\,q_x{}^i\right) + \vec{\mathrm{H}}^e \cdot \int x\dot{\vec{\mathrm{B}}}^i\,dv + \vec{\mathrm{E}}^e \cdot \int x\dot{\vec{\mathrm{D}}}^i\,dv,$$

$$\vec{\mathrm{G}} = \vec{\mathrm{G}}^i + (\vec{\mathrm{E}}^e \times \int \vec{\mathrm{H}}^i\,dv) - (\vec{\mathrm{H}}^e \times \int \vec{\mathrm{E}}^i\,dv),$$

$$\int_\infty x(\vec{\mathrm{S}}\cdot\vec{n})\,d\sigma = -\vec{\mathrm{E}}^e \cdot \int x\,\dot{\vec{\mathrm{D}}}^i\,dv + [\vec{\mathrm{E}}^e \times \int \vec{\mathrm{H}}^i\,dv]_x$$

$$-\vec{\mathrm{H}}^e \cdot \int x\,\dot{\vec{\mathrm{B}}}^i\,dv - [\vec{\mathrm{H}}^e \times \int \vec{\mathrm{E}}^i\,dv]_x$$

$$-(\vec{\mathrm{E}}^e \times \vec{m})_x.$$

Substituting this into the equation mentioned, we get with regard to (5, 34*a*)

$$(5, 35)\quad \mathrm{E}\,\dot{\vec{q}}^i = \vec{\mathrm{E}}^e \times \vec{m}.$$

(5, 27), (5, 28), (5, 34) and (5, 35) are the equations of motion in the rest-system of the singularity.

To write them in a general coordinate system with velocity $\vec{v}$, we refer the angular momentum $\vec{\mathrm{M}}^i$ and the centre $\vec{q}^i$ to the singularity $\vec{r}_0$ as origin (*i.e.*, we take $\vec{r}_0 = 0$); then we introduce the space-time 4-vector

$$(5, 36)\quad (\vec{\mathrm{G}}^i, \mathrm{E}^i) = (g_1, g_2, g_3, g_4),$$

and the space-time 6-vectors

$$(5, 37)\quad \begin{cases} (\vec{\mathrm{B}}^e, \vec{\mathrm{E}}^e) = (\mathrm{F}_{23}, \mathrm{F}_{31}, \mathrm{F}_{12}\,;\, \mathrm{F}_{14}, \mathrm{F}_{24}, \mathrm{F}_{34}), \\ (\vec{m}, \vec{p}) = (m_{23}, m_{31}, m_{12}\,;\, m_{14}, m_{24}, m_{34}), \\ (\vec{\mathrm{M}}^i, \vec{\mathrm{P}}^i) = (\mathrm{M}_{23}, \mathrm{M}_{31}, \mathrm{M}_{12}\,;\, \mathrm{M}_{14}, \mathrm{M}_{24}, \mathrm{M}_{34}); \end{cases}$$

$\vec{p}$ and $\vec{\mathrm{P}}^i$ are defined by

$$(5, 38)\quad \begin{cases} \vec{p} = \vec{m} \times \vec{v}, \\ \vec{\mathrm{P}}^i = \mathrm{E}^i\,\vec{q}^i. \end{cases}$$

Further we observe, that

$$(5, 39)\quad Q_k{}^l = f^{ln}m_{nk} - f^{kn}m_{nl}$$

is an antisymmetric tensor.

The covariant components Q_{kl} are

$$(5, 40)\quad (Q_{23}, Q_{31}, Q_{12}) = (\vec{B}^e \times \vec{m}) - (\vec{E}^e \times \vec{p}),$$

$$(5, 41)\quad (Q_{14}, Q_{24}, Q_{34}) = (\vec{E}^e \times \vec{m}) + (\vec{B}^e \times \vec{p}).$$

Now the equations of motion can be written

$$(5, 42)\quad \begin{cases} \dot{g}_k = e F_{kl} \dot{q}^l, \\ \dot{M}_{kl} = Q_{kl}, \end{cases}$$

where the dot means differentiation with respect to proper time; or in space-vector notation [omitting the indices (e) and (i)]:

$$(5, 43)\quad \begin{cases} \dfrac{d\vec{G}}{dt} = e\left(\vec{E} + (\vec{v} \times \vec{B})\right), \\ \dfrac{dE}{dt} = e\,\vec{v}\cdot\vec{E}; \end{cases}$$

$$(5, 44)\quad \begin{cases} \dfrac{d\vec{M}}{dt} = (\vec{B} \times \vec{m}) - (\vec{E} \times \vec{p}), \\ \dfrac{d\vec{P}}{dt} = (\vec{E} \times \vec{m}) + (\vec{B} \times \vec{p}); \end{cases}$$

$$(5, 45)\quad \begin{cases} \vec{p} = \vec{m} \times \vec{v}, \\ \vec{P} = \vec{E}q. \end{cases}$$

6. *Conclusion.*

The equations (5, 44) and the first of (5, 45) are those given by Kramers;[6] the second equation (5, 45) gives the physical interpretation of the quantity $\vec{P}$, introduced by Kramers quite formally, as the product of energy and the distance of the centre of energy from the singularity. The results of Kramers' paper hold also in our theory: quantisation of the angular momentum leads to Dirac's wave-equation for the electron, and the ratio of magnetic moment to angular momentum is e/μ, where μ is the rest-energy. But one meets deep difficulties in trying to interpret these results on the basis of the unitary field theory. It seems very probable and can be confirmed by strong arguments, that the high rest-energy of the heavy elementary particles, neutron and proton, is of magnetic origin.[7] But there seems to be no solution of the field equations corresponding to a pure magnetic dipole. These questions will be discussed later.

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[6] H. A. Kramers, *loc. cit.*

[7] M. Born, *Nature*, 1935, **136**, 952; *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 533.

THE RAMAN SPECTRA OF ORTHO-PHOSPHORIC ACID AND SOME PHOSPHATES.

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1. Introduction.

In a recent communication to these *Proceedings*,[1] the author studied the progress of electrolytic dissociation and the effect of polymerisation on the Raman spectrum of iodic acid. This investigation has been extended to other inorganic acids and the present paper deals with the results obtained with ortho-phosphoric acid (H_3PO_4). The Raman spectrum of this acid has been investigated by Nisi[2] who obtained frequency differences* of 356, 498 and 911 for 84% , 512 and 906 for 50% and 505 and 895 for 25% solutions. These results have been confirmed quite recently by Jeppesen and Bell.[3] But in spite of the attempts of several workers to obtain the Raman spectra of the three series of salts of this acid corresponding to the stepwise substitution of the three hydroxyl hydrogen ions, it is surprising that only two of them have so far yielded positive results. Nisi obtained four lines at 358, 518, 889 and 1061 for a 38% solution of dihydrogen-sodium phosphate and Schæfer and his co-workers[4] observed one line at 924 for the crystals of the tertiary phosphate of ammonium. Thus the Raman spectra studies of this acid and its salts are obviously incomplete.

2. Experimental Arrangements.

One of the chief difficulties experienced by the earlier investigators in obtaining the Raman spectra of phosphoric acid[5] and the phosphates is the strong continuous spectrum which appears on every plate and masks all faint lines. As mentioned in the previous communications, the pyrex mercury arc designed and used by the author gives much less background than the quartz burners usually employed and have been helpful for giving

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[1] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 119.
[2] Nisi, H., *Jap. Jour. Phys.*, 1929, **5**, 119.
* The numbers in this and the following pages denote frequency shifts in cm^{-1}.
[3] Jeppesen, M. A., and Bell, R. M., *Jour. Chem. Phys.*, 1935, **3**, 363.
[4] Schæfer, Matossi and A derhold, *Zeit. f. Phys.*, 1930, **65**, 289.
[5] Hibben, J. H., *Jour. Amer. Chem. Soc.*, 1931, **53**, 2418.

the very long exposures that are necessary in the present work. The constructional details of the arc are given in Fig. 1. Three electrodes A, B and C

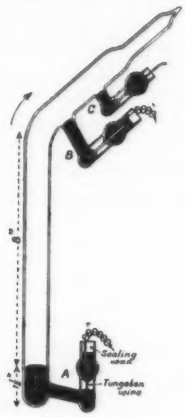

FIG. 1.

are joined to a thick walled pyrex tube of $\frac{3}{4}$" diameter and 12" long which is bent to the form illustrated. After the introduction of freshly distilled mercury, the tube is evacuated thoroughly for about six hours while the arc is kept running hot and finally sealed off at a vacuum higher than 10^{-5} mm. The electrodes A and C are connected to an induction coil for starting the arc and A and B are connected to 220 volt mains through a rheostat in the usual manner. The arc is run in the vertical position and the mercury distilling from it fills the cathode at the top and overflows, thus keeping a constant level for the cathode. The electrode C may also be dispensed with and the arc started by tilting it in the direction of the arrow. These lamps are found to be very efficient for recording faint lines in crystals and solutions, where the intensity of the unmodified light is enormously great and are quite reliable for continuous use. A slow stream of air directed to the top alone helps to diminish the continuous spectrum further. The general experimental method is the same as for the previous investigations of the author.

3. Results.

The purest sample of ortho-phosphoric acid supplied by E. de Hæn was used as such and its Raman spectrum was obtained for a wide range of concentrations varying from 85% (by weight) to 3%. The product of the time of exposure and the concentration was kept constant throughout. The results are given in Table I. The intense line which appears at all concentrations gradually shifts from 914 to 876 in passing from 85% to 3% solution.

TABLE I.

Ortho-phosphoric Acid H_3PO_4.

Concentration (% by weight)	Raman lines in cm^{-1}							Remarks
85%					914 st	495 v.w,d	361 v.w,d	Strong continuous spectrum
60%					903 st	495 w,d	361 v.w,d	„
30%	..	1200	—— (band)	950	890 v.st	495 m,d	361 w,d	Water bands appear
15%	1427 v.w	1194 w,d	1082 w	959 w	886 v.st	495 w,d	361 w,d	Water bands strong
7·5%	1427 v.w	1194 w,d	1082 w	959 w	886 st	495 w,d	361 v.w,d	
3%	..	..	1082 v.w	959 v.w	880 st	..	..	„

st=strong; *v.st*=very strong; *m*=medium; *w*=weak; *v.w*=very weak; *d*=diffuse.

It is also qualitatively observed that the intensity of this line increases as the concentration falls off to about 10%. Two other weak and diffuse lines at 495 and 361 appear unshifted at all concentrations. A broad but weak band with a frequency shift of about 950–1200 makes its appearance at about 30% and breaks up into three weak and diffuse lines of frequency differences of 1194, 1082 and 959. Due to the extreme feebleness of these lines their intensity variations on dilution could not be determined. A spectrum of the acid taken with *p*-nitro-toluene as filter to cut off the 4047 radiations, shows a faint line at 1427. The water bands at 3220, 3435 and 3596 brighten up as the dilution increases and the intensities of the bands at 3220 and 3435 are also greater than for the pure water. The increase in the intensity of 3220 is evidently due to the superposition of the weak line at 1427 on this band and the intensity of 3435 is probably enhanced by the vibrations of the OH groups in the acid itself.

Phosphates.—The crystals of the secondary and tertiary phosphates of sodium, potassium and ammonium were prepared from the corresponding primary salts by the addition of the calculated amount of alkali and purified by repeated crystallisations. The results are given in Table II. The crystals yielded only very weak lines even on prolonged exposure and except in the case of tertiary phosphates, their Raman lines are not included in the Table. The exposure time for the aqueous solutions varied from 24 hours to 48 hours.

TABLE II.

Phosphates.

Substance	Raman lines in cm^{-1}					Crystal
Na_3PO_4 17%	1085 v.w	971 m	..			956 w
K_3PO_4 20%	..	984 m	944 m,d			966 w 944 w
$(NH_4)_3PO_4$ 31%	1080 v.w	985 m	..	515 v.w	363 v.w	951 w
Na_2HPO_4 17%	1085 w	971 m	886 v.w	..	..	
K_2HPO_4 17%	1070 w	965 st	889 w	..	..	
$(NH_4)_2HPO_4$ 30%	1070 w	975 st	889 w	515 v.w	363 v.w	
$NaNH_4HPO_4$ 20%	1085 w	975 m	889 v.w	515 v.w	..	
NaH_2PO_4 27%	1085 m	..	886 st	495 w	356 w	
KH_2PO_4 20%	1080 m	..	869 st	510 w	360 w	
$NH_4H_2PO_4$ 30%	1090 m	..	885 st	515 w	360 w	

4. Discussion of Results.

From the results obtained for the three series of salts of phosphoric acid it is to be inferred that while the three lines at 1085, 495 and 356 appear more or less in the same position in all cases, the intense line shifts from about 885 in the primary salt to about 985 in the secondary and tertiary salts. In the secondary salts the line at 886 is also feebly present. The intensity of the line at 1085 varies from a medium strength in the dihydrogen phosphates to weak in the secondary salts and is very weak in the tertiary salts. These results show that 1085, 980 (*st*), 515 and 363 are the characteristic frequencies of the PO_4 radical 1080, 975(*st*), 889 (*w*), 515 and 363 of the HPO_4'' ion and 1085, 885 (*st*), 515 and 360 of the H_2PO_4' ion. In the Raman spectrum of the acid, the strongest line which is present even in the lowest concentration, namely 3%, is the one at about 889, which indicates, as shown by Nisi,[6] that H_2PO_4' ions predominate at all dilutions. This line is, however, strongly influenced by the concentration of the acid as is shown by a shift of about 34 wave-numbers while passing from 85% to 3%. The appearance of the band between 950–1200 at a concentration of 30% and its further splitting up into three lines in lower concentrations, two of which, namely, 959 and 1082, correspond to those of HPO_4'' ion, suggests that the further ionisation

[6] Nisi, H., *loc. cit.*

of $H_2PO_4' \rightarrow H' + HPO_4''$ begins at this stage. This band may be present also at higher concentrations and is probably masked by the continuous spectrum. The percentage of ionisation from $H_2PO_4' \rightarrow HPO_4''$ remains, however, low even in very dilute solutions as is shown by the weakness of the line at 975. These facts are also in agreement with other physico-chemical measurements.[7] The weak line at 1427 and the increased intensity of the water band at 3435 are, as indicated earlier, due to the OH in the structure of the incompletely ionised acid.

5. *The Structure of Phosphates.*

In Table III, the Raman frequencies ascribed to the PO_4 radical are compared with those of sulphates and selenates.[8] The force constants calculated on the basis of Dennison's dynamical theory are also given. It can be seen from these results, that a close correspondence exists between the frequencies and the force constants of these three radicals indicative of a

TABLE III.

Ion	Raman lines in cm^{-1}				$f \times 10^{-5}$	$f' \times 10^{-5}$	$P \times 10^{-5}$
	ν_1	ν_2	ν_3	ν_4			
PO_4^{---}	985	361	1085	515	5·23	0·967	0·185
SO_4^{--}	983	342	1115	623	4·57	1·14	0·74
SeO_4^{--}	835	447	875	415	4·22	0·59	0·51

tetrahedral structure for the PO_4''' ion as in the case for the SO_4''. The infra-red measurements[9] of lithium phosphate give reflection maxima at about $9 \cdot 25\mu$ and $16\mu - 19 \cdot 1\mu$ which correspond fairly closely to the active frequencies 1085 and 515 in the Raman effect. But the slight variations in the frequency shift, 980, of the symmetrical oscillation in the presence of different cations, namely, potassium, sodium and ammonium, are probably due to a small deviation from the tetrahedral symmetry.

In conclusion, the author wishes to thank Prof. Sir C. V. Raman for his interest in the work.

[7] Mellor, *Treatise of Inorganic Chemistry*, Vol. VIII.

[8] Ganesan, A. S., *Proc. Ind. Acad. Sci.*, A, 1934, 1, 156.

[9] Langford, G., *Phys. Rev.*, 1911, 33, 137.

Summary.

The Raman spectra of ortho-phosphoric acid for a wide range of concentrations and of the primary, secondary and tertiary phosphates of sodium, potassium and ammonium have been obtained. The acid has yielded new lines which indicate the ionisation of $H_3PO_4 \rightarrow H^\circ + H_2PO_4'$ and the further ionisation of $H_2PO_4' \rightarrow H^\circ + HPO_4''$. Weak lines characteristic of the OH oscillations have also been observed for the acid. The three series of phosphates give characteristic spectra which are identified as due to H_2PO_4', HPO_4'' and PO_4''' ions. The frequency shifts of the PO_4 radical are compared with those of SO_4 and SeO_4 and the force constants are evaluated.

THE OCCURRENCE OF FURAN DERIVATIVES IN VOLATILE OILS—III.

β-Clausenan and γ-Clausenan.

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and

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The volatile oil from the leaves of *Clausena Willdenovii*, W. and A. collected in winter has been shown to consist of three new compounds, α-, β- and di-α-clausenans belonging to the furan group.[1] The leaves of the same plant grown in a different locality and collected at the same time of the year, however, yielded a similar product but without any appreciable quantities of α-clausenan. The analytical constants of the three new oils (III, IV and V) and of the two previous samples (I and II) have been given in Table I and indicate apparent identity between them. The constants for the product obtained by extraction of the distillation water which dissolves out mainly the pleasant smelling esters have also been given. The new samples on fractionation behave like the previous specimens, as shown in Table II, three groups of products being obtained 104°/50 mm., 80–125°/10 mm., 190°/10 mm. The first fraction was found to be a mixture of β-clausenan and a new body hereafter called γ-clausenan which is the main constituent and is a clear colourless liquid having an odour of unripe mangoes. The next fraction consisted mainly of esters and ketones and the last of di-α-clausenan.

According to Wienhaus[2] the atomic refraction constant for furan oxygen is 1·2, being lower than for ethereal oxygen (1·642) in most other compounds. The molecular refractions of the clausenans taking the usual value and Wienhaus's constant are as follows:

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[1] *Proc. Ind. Acad. Sci.*, 1934, **1**, 186.

[2] *Ber.*, 1920, **53**, 1660.

	d_4^{30}	n_D^{30}	$(R_L)_D$ Found	$(R_L)_D$ Calculated	
				O=1·643	O=1·2
α-Clausenan	0·9026	1·4722	45·96	45·96	45·51
γ-Clausenan	0·9050	1·4739	45·98	45·96	45·51
Di-α-Clausenan	1·0196	1·5468	89·95	90·18	89·29

It is found that the values are in good agreement with the usual value for ethereal oxygen. It has also been observed by Eisenlohr that the depression of molecular refraction observed in furan and pyrone decreases in their dimethyl derivatives and it is possible that in the higher homologues, this depression vanishes and the usual value for ethereal oxygen becomes valid.

The parachor was found to be 382·8 at 30° and 387·8 at 50° the calculated value being 386·8, the higher value at 50° indicating that γ-clausenan is an associated liquid. It has nearly the same viscosity as α-clausenan. The vapour pressures between 80–180°, Ramsay and Shield's constant and other properties have been determined and will be found in the experimental part. Dioxan was found to be unsuitable as a solvent for molecular weight determination of these compounds.

Pure γ-clausenan keeps well in the absence of oxygen and is miscible with most organic solvents. It has somewhat higher physical properties and differs from α- and β-clausenans in not forming an addition compound with either ferrocyanic or ferricyanic acids. It could be easily separated and purified by this process from β-clausenan with which it is mixed up. While α-clausenan was uneffected by sodium and alcohol, the γ-isomer was reduced to a tetrahydro-derivative. The reduction product gave the Liebermann colouration and with bromine in chloroform solution, the same colour changes as those observed with α-clausenan, showing the presence of the furan nucleus. No ketone was obtained by oxidation with potassium permanganate, as in the case of α-clausenan. Like most furan compounds γ-clausenan is also gradually resinified in the presence of acids and is uneffected by boiling acetic anhydride, alkalis and water. As γ-clausenan does not react with ferrocyanic acid, it was possible to obtain β-clausenan pure. Its properties along with those of its acetyl derivative have been described.

Experimental.

The analysis of oils obtained from three lots of leaves collected in winter from a different locality and immediately distilled have been given in Table I (III, IV and V), along with constants, for the samples previously examined, which show that they are similar.

TABLE I.

Sample No.	III	IV	V	I	II
d_{30}^{30}	0·9349	0·9333	0·9340	0·9317	0·9341
n_D^{30}	1·5129	1·5114	1·5112	1·5114	1·5112
$[\alpha]_D^{30}$	−1·6°	−2·1	−1·9	−1·1	−0·2
Acid value	0·3	0·2	0·4	0·4	1·2
Ester value	9·5	9·1	9·1	9·2	13·4
Acetyl value	22·2	23·7	20·1	13·2	24·4

Appreciable quantities of the oil were dissolved in the distillation water. The oil (10 g.) extracted from 8 litres of distillation water had the following properties : d_{30}^{30}, 1·086 ; n_D^{30}, 1·5182 ; acid value, 7·9 ; ester value, 220·1. The esters appear to be particularly soluble in water.

Distillation of the oil.—The oil (sample III ; 490 g.) was fractionated three times with an eight pear Young's column at 50 mm. in the first stage, and at 10 mm. later from a Claisen flask, the following fractions being obtained :

TABLE II.

Fraction	B.P.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Weight in grams	Yield per cent. on original oil
1	101—103°/50 mm.	0·8984	1·4832	+ 0·9°	50	10·2
2	103—104	0·9107	1·4840	+ 0·4	100	20·4
3	104—105	0·9152	1·4882	+ 0·4	170	34·7
4	84—87/10 mm.	0·9226	1·4914	± 0	20	4·1
5	87—105	0·9304	1·5108	− 8·6	10	2·0
6	105—185	0·9350	1·5140	−18·2	5	1·0
7	188—193	1·060	1·5466	—	130	26·5

TABLE III.

γ-Clausenan		β-Clausenan	
Temperature °C.	Vapour pressure mm.	Temperature °C.	Vapour pressure mm.
82·0	27·0	70·0	19·5
95·0	44·0	85·0	38·0
102·0	52·5	97·0	65·5
112·0	74·0	99·0	72·0
119·5	106·5	104·0	82·0
125·5	127·0	125·0	172·0
129·0	145·0	131·0	207·5
135·0	180·0	138·0	258·0
139·0	210·0	148·0	348·0
143·0	235·0	154·0	412·5
144·5	265·0	158·0	458·0
151·0	314·0	161·0	496·0
156·0	360·0	168·0	597·0
159·0	394·0	171·0	644·0
163·5	449·0	174·0	696·0
165·5	474·5	176·0	734·5
171·0	548·0		
173·0	585·0		
175·0	607·5		
177·5	647·0		
180·0	684·0		

β-Clausenan.—Since the new samples were free from α-clausenan, it seemed possible that β-clausenan will be more easily obtained pure as the other compounds accompanying it do not react with ferrocyanic acid. Fraction I was treated with pure ferrocyanic acid and the addition compound decomposed with sodium carbonate and the liberated product was fractionated over sodium when β-clausenan having the following properties was obtained : b.p. 96–97/50 mm. ; d_{30}^{30}, 0·8805 ; d_4^{30}, 0·8768 ; d_{50}^{50}, 0·8701 ; d_4^{50}, 0·8589 ; $[\alpha]_D^{30}$, + 3·0 ; n_D^{30}, 1·4681 ; γ_{30}, 27·4 ; γ_{50}, 27·2 ; η_{30}, 0·090. Analysis : C, 79·46 ; H, 9·9 ; $C_{10}H_{14}O$ requires C, 80·0 ; H, 9·33. The vapour pressures have been given in Table III.

The parachor was 396·8 at 30° and 403·9 at 50° in fair agreement with the calculated value 397·4 according to Mumford and Philips and 406·4 according to Vogel.

Acetylation of β-clausenan.—β-Clausenan (5 g.) was boiled for an hour with acetic anhydride (10 c.c.) and sodium acetate (1·0 g.). The acetylated product distilled at 105°/32 mm. ; d_{30}^{30}, 0·9481 ; n_D^{30}, 1·4672 ; acetyl value 265, showing that the sample is quantitatively acetylated. Though β-clausenan is not as unsaturated as α-clausenan, it is more amenable to resinification and oxidation.

γ-Clausenan.—The major portion of the fractions failed to react with freshly prepared ferrocyanic acid. The unreacted portion (270 g.) on fractionation over sodium was found to be homogeneous and had the following properties given in (*a*), and (*b*) gives the properties of α-clausenan for comparison :

	B.P. at 50 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	$(R_L)_D$
(*a*)	103–104°	0·9089	1·4739	nil	45·98
(*b*)	102	0·9065	1·4722	,,	45·96

Analysis of (*a*) : C, 81·70 ; H, 8·40 ; $C_{10}H_{12}O$ requires C, 81·81 ; H, 8·18. It is not identical with α-clausenan having somewhat higher physical properties and is hereafter called γ-clausenan. It is uneffected by boiling with acetic anhydride, alkalis or water in a sealed tube. It gives the Liebermann test and with an acetic acid or chloroform solution of bromine, gives a purple colouration changing to blue and finally green, being similar in these respects to α-clausenan. Unlike the latter, however, γ-clausenan does not combine with ferrocyanic or ferricyanic acids.

Viscosity and surface tension of γ-clausenan.—They were measured by means of an Ostwald viscometer calibrated with benzene at 30° as in the case of α-clausenan. The time of flow for γ-clausenan was 105 seconds, being an average of four readings. The viscosity was found to be 0·0085 c.g.s.

The difference in the equilibrium levels in the capillary limb and the lower viscometer bulb was 29·6, 28·8 and 64·2 and 61 mm. for γ-clausenan and water respectively giving a surface tension of 29·92 at 30° and 29·10 at 50°.

The parachor was found to be 382·8 at 30° and 388·0 at 50°, the calculated values being 386·8 from Mumford and Philips and Vogel's data.[3]

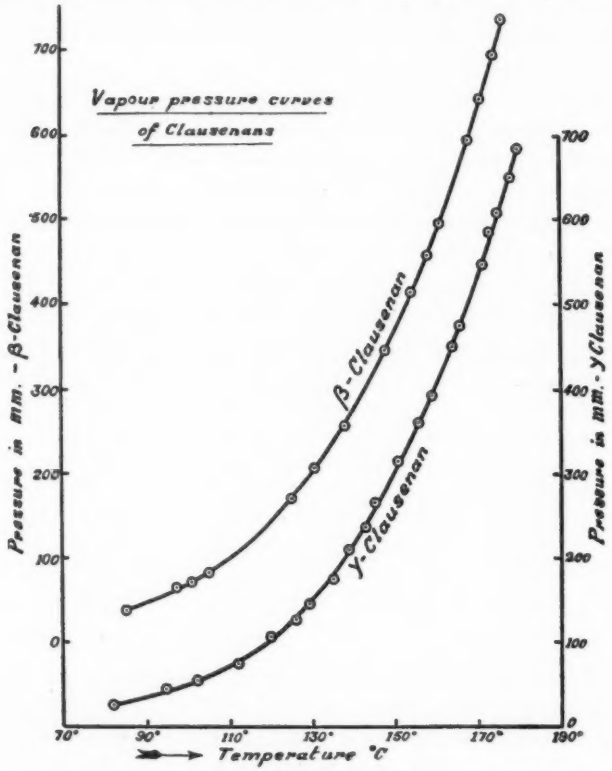

FIG. 1.

The molecular refraction was found to be 45·98, identical with the calculated value 45·96, taking for the furan oxygen Eisenlohr's value 1·643

[3] *J. C. S.*, 1929, **130**, 2112; 1934, **135**, 334.

for ethereal oxygen. If Wienhaus's value 1·2 is taken for the furan oxygen, the value for molecular refraction is depressed by 0·44.

The Ramsay and Shield's constant was found to be somewhat high being (*a*) 2·43 by application of Ramsay and Shield's equation, (*b*) 2·46 by Walden and Swinne's method.[4] The critical temperature by Guldberg rule is 412°. The molecular latent heat of vapourisation from Trouton's rule modified by Wartenburg[5] ($L = 7 \cdot 4T \times \log T$) was found to be 10,650 calories at 30°. The value from the formula

$$L = \frac{1 \cdot 985 T_1 T_2}{T_2 - T_1} l_n \frac{p_2}{p_1}$$

based on Clausius-Clapeyron equation was 10,730 calories at 98°C. The molecular volume, using Kopp's constants was 183·8, the experimental value being 148/0·7884 or 186·3.

The vapour pressures of γ-clausenan between 80-180° have been measured by the submerged bulb method of Smith and Menzies[6] and the values recorded in Table III. Fig. 1 shows the vapour pressure curves of the clausenans.

Reduction of γ-Clausenan.—On reduction with sodium and alcohol tetrahydro-γ-clausenan having the following properties was obtained: b.p. 105/100 mm.; d_{30}^{30}, 0·8957; n_D^{30}, 1·4698; C, 78·72; H, 10·22; $C_{10}H_{16}O$ requires C, 78·95; H, 10·52. α-Clausenan was not reduced by this process.

Oxidation with potassium permanganate.—No trace of the ketone $C_9H_{10}O$ obtained from α-clausenan was formed. The products were exclusively acidic and resinous and were not further examined.

Summary.

The analyses of three samples of the volatile oil from *Clausena Willdenovii*, W. & A. have been given. A component $C_{10}H_{12}O$, called γ-clausenan, isomeric with α-clausenan and belonging to the furan group has been isolated from the oil. Its physical properties as well as methods for separating it from α- and β-clausenans have been described. β-clausenan has been obtained pure and its properties determined.

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[4] *Z. Physik. Chem.*, 1913, **82**, 290.

[5] *Z. Electrochem.*, 1914, **20**, 444.

[6] *J. Am. Chem. Soc.*, 1910, **32**, 1448.

BRUCINE SULPHATE AS AN INTERNAL INDICATOR IN TITRATIONS WITH STANDARD DICHROMATE SOLUTION.*

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and
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Received May 2, 1935.

The elegant method of determining iron volumetrically with permanganate cannot be employed in the presence of hydrochloric acid except after the addition of manganous sulphate and phosphoric acid. This procedure, however, has not found general favour and in spite of the disadvantage in the use of an external indicator, dichromate method has more or less been universally adopted. The discovery of diphenylamine as an internal indicator in such titrations (Knop, 1924) was therefore a great advance in this field. This substance gives an intense blue colour when treated with a drop of 0·1 normal solution of potassium dichromate in hydrochloric acid or sulphuric acid containing trivalent iron. The addition of excess of ferrous salt decolourises the indicator so that back titration is possible. Recently Phenanthroline has been studied in detail as an indicator in oxidimetry (Walden and Edmonds, 1935) and has been found to be very satisfactory. But the difficulty with which it is synthesised is for the present against its widespread use.

Though with a strict adherence to the optimum conditions (Sarver, 1927) one may obtain satisfactory results with diphenylamine, there are certain drawbacks in its use. In the presence of the green colour of the chromic salt and the yellow of the ferric salts the end point frequently ceases to be sharp and considerable difficulty is experienced in judging it even after the addition of phosphoric acid. An indicator giving a more easily detectable colour, which is not masked by the chromic or ferric salts, should be more valuable and one such has been found in Brucine. 1 c.c. of a 1 per cent.

* After our work described in this paper had been completed, it was realised that the use of Brucine as an internal indicator had been indicated by Seikichi Miyagi (*J. Soc. Chem. Ind. Japan* 36, supple. binding 1933, 146–47). Since, however, the Japanese author had not examined the scope of the method in detail, we thought it would be useful to publish our results. —T. R. S.

solution of brucine in 100 c.c. of water containing sulphuric acid is coloured a distinct red with one drop of N/100 dichromate solution : this red colour is quite easily visible in the presence of chromic and ferric salts and there is no need to add phosphoric acid as in the case of diphenylamine indicator in order to improve the sharpness of the end point.

The indicator solution is prepared by dissolving one gram of brucine in 100 c.c. of 3 N sulphuric acid and preserved in a stoppered amber coloured bottle. The colourless solution turns pale brown on standing without however losing its usefulness. It is not desirable, however, to prepare more than 100 c.c. at a time. It is further noticed that the indicator functions best only after standing for a few hours after it has been made. Its use in the different methods employing dichromate titrations is illustrated below. 10 drops of the brucine solution are used as indicator. When titrating ferrous salts against dichromate, near the end point—within 3 drops of it—the solution changes to a dirty green and with the first excess drop of dichromate the solution becomes red. The faintest trace of red is easily detected in the presence of the green chromic salt. It is necessary that the acid strength of the solutions is not allowed to fall below 2 normal, though above that it may be allowed to vary within wide limits. Back titration using this indicator is not quite sharp probably due to the oxidation product not undergoing reduction easily.

TABLE I.

Wt. of Ferrous am. sulphate in grams	Vol. of 0·1015 N $KMnO_4$ in c.c. (*a*)	Vol. of 0·1 N Dichromate in c.c. (*b*)	Fe calculated in grams	
			From (*a*)	From (*b*)
0·2025	5·05	5·15	0·0286	0·0288
0·4104	10·05	10·20	0·0570	0·0570
0·6060	15·15	15·35	0·0858	0·0857
0·9015	22·60	23·00	0·1280	0·1284
1·2500	31·25	31·70	0·1771	0·1770
1·8050	45·25	46·00	0·2564	0·2569

Table I compares the results obtained by titrating varying amounts of ferrous ammonium sulphate against standard permanganate on the one hand, and dichromate using brucine sulphate as internal indicator on the other.

The agreement between the two methods is quite close. The colour due to the ferric iron does not affect the sharpness of the end point and this

is further confirmed by adding known large quantities of ferric chloride to the ferrous salt solution that has to be titrated.

TABLE II.

Concentration of dichromate solution 0·1 *N.*
Concentration of ferric chloride 0·2 *N.*
Concentration of ferrous ammonium sulphate 0·1 *N.*

Vol. of $FeCl_3$ added in c.c.	Vol. of Ferrous am. sulphate in c.c.	Vol. of water in c.c.	Vol. of 0·1 N dichromate required in c.c.
10·0	25·0	70	25·00
20·0	25·0	60	25·05
40·0	25·0	40	25·05
80·0	25·0	..	25·05

The indicator is therefore useful in the estimation of chrome-iron alloys and ores in which the ferric iron is present in large quantities and has been utilised by us for the analysis of the ore.

Mercuric chloride, mercurous chloride and stannic chloride do not affect the end point and this was settled by analysing a ferric chloride solution in two ways :— (1) the iron was precipitated as ferric hydroxide, filtered, washed and dissolved in 1 : 1 sulphuric acid and after reduction with arsenic-free zinc titrated against standard permanganate ; (2) the solution was reduced with stannous chloride, excess of the stannous salt oxidised with mercuric chloride and then titrated against potassium dichromate using brucine sulphate as indicator. The comparative results are given in Table III and they are very concordant.

TABLE III.

Vol. of $FeCl_3$ in c.c.	0·1015 N permanganate in c.c. (1)	0·1 N dichromate in c.c. (2)	Amount of iron present in grams	
			From (1)	From (2)
10·0	16·95	17·30	0·0961	0·0966
10·0	17·00	17·25	0·0963	0·0963
25·0	42·60	43·25	0·2415	0·2414
25·0	42·45	43·20	0·2410	0·2417

The above fact was further proved by analysis of samples of Kahlbaum's purest specimen of iron wire. The wire was converted into ferric chloride and the iron estimated as above using dichromate and brucine.

TABLE IV.

Wt. of iron wire in gms.	0·1143	0·1365	0·1893	0·2632
0·1 N $K_2Cr_2O_7$ in c.c. ..	20·50	24·40	33·90	47·10
Fe%	100·1	99·82	100·0	99·90

Titration of ferrous iron in the presence of hydrochloric acid with permanganate is possible when diphenylamine is used as indicator and brucine can be employed for the same purpose with equal advantage. Chlorine that may be liberated from hydrochloric acid affects the indicator just as any other oxidising agent and acts as so much permanganate. Table V records data obtained to illustrate this aspect of the use of brucine.

TABLE V.

Ferric chloride solution reduced with stannous chloride etc., and titrated against 0·1015N potassium permanganate.

Vol. of Ferric chloride soln. in c.c.	Vol. of Pot. permanganate in c.c.	Amount of iron	
		Found in gm.	Taken in gm.
10·0	16·90	0·0958	0·0965
10·0	17·00	0·0963	0·0965
25·0	42·55	0·2412	0·2415
25·0	42·50	0·2409	0·2415

Application to soil analysis.—As a rapid approximate method for the estimation of soil organic matter Schöllenberger (1927) recommends the oxidation of the organic matter with excess of chromic acid and estimation of the excess of the oxidant by titration with ferrous ammonium sulphate using diphenylamine as indicator. It is now found that brucine can be used for the purpose with advantage. After the oxidation is over, the chromic acid solution is diluted, a known excess of ferrous ammonium sulphate solution is added and the excess of the ferrous salt titrated against standard dichromate. Direct titration of the chromic acid with ferrous sulphate is not possible with

brucine as indicator and is not very advisable even with diphenylamine since undesirable oxidation products are formed. Concordant results are obtained with brucine as shown below :—

TABLE VI.

	Wt. of soil sample	Per cent. C-content	Deviation from the Mean
A. Low Grade	0·5005	2·50	−0·03
	0·3080	2·48	−0·05
	0·4254	2·60	0·07
	Mean	2·53	
B. High Grade	0·3412	5·06	0·05
	0·4215	5·02	−0·01
	0·3915	4·96	−0·05
	Mean	5·01	

Summary.

Brucine sulphate has been shown to be a good internal indicator for titrations with dichromate and in certain respects superior to diphenylamine. The colour change from green to bright red at the end point is much more pronounced than the change from green to blue in the case of diphenylamine.

It has been shown that in titrations with potassium permanganate solutions, the disturbing effects due to the presence of hydrochloric acid may be obviated by using brucine as an internal indicator. The presence of ferric iron has not been found to interfere with the sharpness of the end point.

The use of this indicator in the analysis of chromium ores and in the estimation of organic matter in soils by the Schöllenberger method has been indicated.

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OPTIC MOMENTS OF ORGANIC MOLECULES IN RELATION TO CRYSTALLINE AND MAGNETIC BIREFRINGENCE.

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1. *Introduction.*

In a previous communication (Ramanadham, 1934), the author had shown how the principal refractive indices of a crystal could be correlated with the principal optic moments of the molecules constituting it and their orientation inside. As a particular case, the optic moments of the naphthalene molecule were deduced on the one hand from the known (1) refractive index, (2) the magnetic birefringence of the substance in the liquid state, and (3) the depolarisation of the light scattered by its vapour, and on the other hand from the observed principal refractive indices of the crystal together with the known orientations of the molecules. Agreement was found to be fair between the sets of optic moments deduced by these two entirely different methods.

It appears desirable to extend this treatment to a number of other organic crystals. As a preliminary to it, has been here undertaken the determination of the magnetic birefringence of organic solids in solution with carbon tetrachloride as the solvent. The choice of the solvent is based on the fact that carbon tetrachloride is known to exhibit no detectable magnetic double refraction. The substances are specially chosen from among those whose magnecrystallic behaviour has been studied by Krishnan.

2. *Experimental.*

The experimental arrangement is the same as that adopted in the author's previous investigations (Ramanadham, 1929). The method of estimation of the positive double refraction exhibited by the aromatic compounds is, however, slightly different in the present arrangement. Instead of compensating the double refraction by compressing a plate horizontally, the compensation is now made more conveniently by elongating a glass plate vertically by weights hung from it. All the measurements are made with respect to benzene and the absolute values calculated by assuming the value of C_M for benzene as 5×10^{-13} at 30° C.

To prepare solutions of definite concentration, a measuring flask of 25 c.c. capacity, provided with a ground-glass stopper, is taken and into it is put a weighed quantity of the substance under investigation. Then carbon tetrachloride liquid is run down from a burette into the flask and after dissolving the substance, the volume of the solution is made up to 25 c.c. by further running down the required amount of CCl_4. At the same time, the total volume of CCl_4 run down is noted.

As the refractive indices of the solutions are required in the calculations, they have been determined with an Abbe refractometer.

3. Results.

The results are exhibited in the following table :—

Substance	Temperature	Weight of the substance in 25 c.c. of the solution	Volume of CCl_4 in 25c.c. of the solution	Refractive index of the solution for the D line	$C_M \times 10^{13}$
Naphthalene	27°·5 C.	2·5 g.	22·5 c.c.	1·4729	3·1
,,	27°·5 C.	4·0 ,,	20·8 ,,	1·4834	4·6
Diphenyl	30° C.	8·0 ,,	17·5 ,,	1·5084	4·0
Acenaphthene	30° C.	3·0 ,,	22·2 ,,	1·4770	1·0
Benzil	32° C.	2·9 ,,	22·5 ,,	1·4728	1·5
Salol	32° C.	7·0 ,,	19·4 ,,	1·4910	2·1
Benzophenone	29° C.	7·0 ,,	19·1 ,,	1·4990	2·1
Phenanthrene	31° C.	2·5 ,,	22·9 ,,	1·4822	3·1

4. Discussion.

(*a*) *Naphthalene.*—It is desired to see how far the observed values of C_M in the case of naphthalene solutions agree with those obtained by Salceanu (1932) in molten naphthalene. In calculating the magnetic birefringence to be expected for naphthalene solutions, we will accordingly make use of the optic moments $b_1 = 25 \cdot 85 \times 10^{-24}$, $b_2 = 22 \cdot 25 \times 10^{-24}$ and $b_3 = 9 \times 10^{-24}$ derived by the author in an earlier paper (*loc. cit.*) on the basis of Salceanu's value of C_M for molten naphthalene.

Applying the formula*

$$C_M = \frac{1}{20} \cdot \frac{n^2 - 1}{n\lambda kT} \cdot \frac{\nu_1[(a_1 - a_2)(B_1 - B_2) + \cdots] + \nu_2[(a_1' - a_3')(B_1' - B_2') + \cdots]}{\nu_1(b_2 + b_2 + b_3) + \nu_2(b_1' + b_2' + b_3')}$$

* This formula for the magnetic birefringence of solutions is taken from M. Ramanadham, *Ind. Jour. Phys.*, 1929, **4**, 109.

the values of C_M for naphthalene solutions at the two concentrations for which observations have been made are calculated and shown below :—

Wt. of the naphthalene in 25 c.c. of the solution	Observed $C_M \times 10^{13}$	Calculated $C_M \times 10^{13}$
2·5 g.	3·1	2·5
4·0 ,,	4·6	3·9

The agreement between the observed and calculated values is fair within the degree of experimental error. In making the calculation, it is assumed that the carbon tetrachloride molecule is optically and magnetically isotropic, that the second term in the numerator vanishes, and that the second term in the denominator becomes $\nu_2 . 3b'$ where b' is the optic moment of the carbon tetrachloride molecule in the gaseous condition ; this can be deduced from the known refractive index of the liquid at the known density by applying Lorentz's equation

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{3}{4\pi\nu} = b'.$$

The values of B_1, B_2, B_3 are obtained from equations of the form $B_1 = b_1(1 + p_1 x)$, where x is the optical susceptibility of the solution. The values of p_1, p_2 and p_3 are the same as those used previously, namely, 1·8, 2·8 and 8·0.

(*b*) *Diphenyl.*—From a study of the magnetic anisotropy of the crystal, Krishnan (1933) has been led to place the length of the molecule at an angle 20°·1 from the C axis and the breadth in the plane of the molecule at 31° to the *b* axis. This orientation has been confirmed by Dhar (1932) by X-ray analysis.

The refractive indices of the crystal are given by Narasimham (1931) as 1·554, 1·586 and 1·647. He has also given certain data regarding the disposition of the principal axes of the optical ellipsoid and the optic axes but these are not consistent amongst themselves. Hendricks and Jefferson (1933) who subsequently repeated the measurements on the crystal found the refractive indices to be 1·5598, 1·6542 and >1·90. These authors do not, however, give any information regarding the disposition of the principal optic axes with reference to the crystallographic axes. Groth has recorded that the optic axes make 20°·75 and 57°·75 respectively with the normal to the 001

face where the interference figure is viewed through cedar oil (Refractive index 1·515).

An attempt is made in the present investigation to decide between the conflicting results regarding the refractive indices and to fix the directions of the principal axes of the optical ellipsoid by making the following observations.

The apparent angle made by one of the optic axes with the normal to the plate is measured as 31° ·8 by mounting the crystal on a Fedorov stage under the microscope and tilting it until the corresponding melatope coincides with the intersection of the crosswires. This reading is in agreement with the angle 20° ·75 given by Groth if we take into account the fact that the latter has been measured under cedar oil of refractive index 1·515.

It is further noticed that the interference figure shown by a diphenyl crystal of thickness 0·109 mm. between crossed nicols exhibits 13 complete rings. The double-refraction in the plate, *i.e.*, in 001 plane becomes then ·0701.

To see which set of refractive indices gives this observed double refraction ·0701 in the (001) plane, the true angles made by the optic axes with the normal are calculated with the aid of each one of the alternative values available for the intermediate refractive index, assuming the apparent angles given by Groth as correct and then the birefringence in the plate from both sets of values† by applying the formula

$$\frac{1}{\alpha'^2} - \frac{1}{\gamma'^2} = \left(\frac{1}{\alpha^2} - \frac{1}{\gamma^2}\right) \cdot \sin\theta \cdot \sin\theta'$$

where α' and γ' denote the principal indices in the plate the normal to which makes the real angles θ and θ' with the optic axes and α and γ denote the minimum and maximum principal refractive indices of the crystal.

$\alpha' - \gamma'$ has come out according to Narasimham's set of values as ·024 and according to those of Hendricks and Jefferson as ·0712. The latter is in satisfactory agreement with the author's observations and hence Hendricks and Jefferson's values are taken as reliable.

We proceed now to fix the orientations of the principal optic axes. The true angles θ and θ' are (from Hendricks and Jefferson's refractive indices and Groth's apparent angles) 18° ·56′ and 50° ·48′. Hence the acute bisectrix which in this case is the direction of maximum refractive index can easily be seen with the aid of the figure to make an angle of 20° ·42′ with the crystallographic C axis in the obtuse angle.

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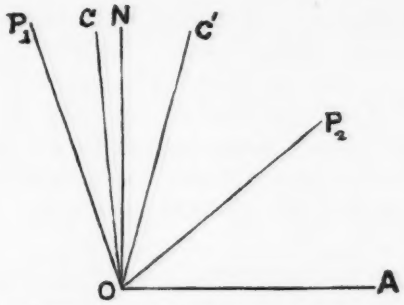
† In the case of values given by Hendricks and Jefferson the maximum refractive index is put equal to 1.90.



OA=A axis; OP_2=Optic axis; OC'=Bisectrix; ON=Normal; OC=C axis; OP_1=Optic axis; $C\hat{O}A=94°46'$; $P_1\hat{O}N=18°56'$; $P_2\hat{O}N=50°48'$; $C\hat{O}C'=20°42'$.

This indeed coincides with the minimum diamagnetic axis and hence the direction in which the length of the molecule lies. Thus it appears that the optics of a suitable monoclinic crystal will enable us to fix the direction of the length of the molecule along which we naturally expect the maximum optical polarisability to occur. Unfortunately the data on the optics of organic crystals are very meagre and where available not quite reliable and so we cannot extend such investigations to other cases.

We now calculate the optic moments b_1, b_2 and b_3 of the diphenyl molecule from the known orientations which are represented in the scheme below and by making use of the formula which the author has derived in the previous paper (*loc. cit.*) for the refractive indices in the principal directions. The values of p_1, p_2 and p_3 are assumed to be 1·8, 2·8 and 8·0 same as those of naphthalene to which assumption we have been led by comparing the dimensions of the unit cell and the angle β in both cases. The density of the crystal is 1·154 (Ashutosh Mukherjee, 1933).

	X	Y	Z
1	0°	90°	90°
2	90°	31°	59°
3	90°	59°	31°

X, Y, Z are respectively the directions of maximum, intermediate and minimum refractive indices. 1, 2, 3 represent respectively the directions of the length, breadth and thickness of the molecule which are mutually at right

angles to one another. $b_1 = 33 \cdot 32 \times 10^{-24}$, $b_2 = 23 \cdot 06 \times 10^{-24}$, $b_3 = 12 \cdot 13 \times 10^{-24}$ c.g.s. units. From Krishnan, we have for the diamagnetic moments $a_1 = -1 \cdot 1039 \times 10^{-28}$, $a_2 = -1 \cdot 1039 \times 10^{-28}$ and $a_3 = -2 \cdot 8828 \times 10^{-28}$ c.g.s. units.

Substituting these values in the formula for C_M for the concentration for which observations have been made, the calculated value of C_M comes out as $4 \cdot 3 \times 10^{-13}$ against the observed value $4 \cdot 0 \times 10^{-13}$ in very close agreement.

The refractive index of the solution can also be calculated by the aid of the formula

$$\frac{n^2 - 1}{4\pi} = \frac{\nu_1(b_1 + b_2 + b_3) + \nu_2(b_1' + b_2' + b_3')}{1 - \frac{1}{3}\nu_1(b_1p_1 + b_2p_2 + b_3p_3) - \frac{1}{3}\nu_2(b_1'p' + b_2'p_2' + b_3'p_3')}$$

which takes into account the anisotropy of the optical polarisation field. The calculated value comes out as 1·522 which is in fair agreement with the observed value 1·5084.

(*c*) *Dibenzyl.*—The magnetic birefringence of this substance has not been studied by the author as it was not available. We can, however, make use of the available data to discuss this case.

The refractive indices of the crystal have been given by Hendricks and Jefferson as 1·7566, 1·6286 and 1·5292. The density of the crystal is 1·0738. The dimensions of the molecule are taken as 11, 11 and 3·8 A.U.‡ for which the values of p_1, p_2, p_3 are calculated in the usual manner.

$$p_1 = p_2 = 2 \cdot 579 \text{ and } p_3 = 7 \cdot 877.$$

Groth's qualitative observations show that the direction of maximum refractive index lies at almost the same direction as the length of the molecule which Krishnan has fixed at an angle of 83°·9 to the C axis. By analogy with diphenyl, we make the assumption that it coincides with the direction

	X	Y	Z
1	0°	90°	90°
2	90°	30°	60°
3	90°	60°	30°

‡ See the diagram given by Dhar, *Ind. Jour. Phys.*, 1934, **9**, 1.

of the length, and since b axis is by virtue of symmetry also the axis of intermediate refractive index, the principal directions of the crystal are easily fixed. The above is the scheme of orientations of the principal axes 1, 2, 3 of the molecule with respect to them.

The values of b_1, b_2, b_3 calculated come out as $b_1 = 32 \cdot 36 \times 10^{-24}$, $b_2 = 28 \cdot 74 \times 10^{-24}$ and $b_3 = 14 \cdot 36 \times 10^{-24}$ c.g.s. units.

The observed refractive index of the liquid dibenzyl at a density of 0·942 grams per c.c. is given as 1·539 (*I.C.T.*, Vol. I) which compares very favourably with 1·535 calculated from the formula

$$\frac{n^2 - 1}{4\pi\nu} = \frac{B_1 + B_2 + B_3}{3}$$

where

$$B_1 = b_1 \left(1 + p_1 \cdot \frac{n^2 - 1}{4\pi}\right).$$

Though this test on the optic moments is not unique, yet a comparison of these values with those of diphenyl shows that they are reliable.

5. *Conclusion.*

In conclusion we point out that the results obtained in the case of diphenyl are significant, showing how the optical properties of a crystal can be a useful check on the X-ray or magnetic analysis of molecular orientation when combined with the knowledge of the magnetic double-refraction, refractivity and depolarisation of the scattered light. At the same time, the validity of the various theories is put to the test. For instance, the theory of magnetic birefringence in regarding it as arising out of the orientation of optically and magnetically anisotropic molecules has found a direct verification in the phenomenon being connected with other independent phenomena, namely, the optical and magnetic anisotropy of crystals. Also the idea of anisotropic polarisation field has consistently been employed. The author's molecular theory of double-refraction of organic crystals has also been put to the test.

The author is highly thankful to Prof. Sir C. V. Raman, Kt., M.A., D.Sc., F.R.S., N.L., for having allowed the use of the strong electromagnet at the Indian Institute of Science, Bangalore, for making some of the observations contained in the present paper. He is also thankful to Mr. S. Bhagavantam for the many useful discussions which the author had with him on the subject. He takes this opportunity also to thank the syndicate of the Andhra University for having awarded him a Research Fellowship at the beginning of this academic year.

Summary.

The results of observations made on the magnetic birefringence of organic solids dissolved in liquid carbon tetrachloride are given. The observed values of C_M for naphthalene solutions are compared with the value of C_M observed by Salceanu on molten naphthalene and found to be in good agreement. The principal optic axes of the diphenyl crystal are fixed on the basis of the author's own observations, those of Groth and also of Hendricks and Jefferson. The direction of maximum refractive index has been found to coincide with the direction which has been assigned to that of the length of the molecule by Krishnan from his diamagnetic observations on the crystal. The optic moments of diphenyl molecule are calculated from the refractive indices and are found to satisfy the observed magnetic birefringence and the refractive index of the solution. The optic moments of the dibenzyl molecule are similarly calculated from the refractive indices and found to agree with the observed refractive index of the liquid dibenzyl.

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VINOGRADOW'S SOLUTION OF WARING'S PROBLEM (II).

By I. Chowla.

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(Communicated by Dr. S. Chowla.)

In the first part of this paper it was shown by the method of Vinogradow, as modified by Pillai, that

Theorem I. If Hypothesis P* *is true, then for* $n > n_0$, *there exists a number* w *depending only on* n *such that every large number* $\equiv 1 \pmod{w}$ *can be expressed as a sum of* $(3n + 2)$ "*nth powers*" $\geqslant 0$.

In the rest of this paper we shall suppose that $n > n_0$. The method of my first paper enables us to formulate the more general

Theorem II. It is possible to find a number w *depending only on* n *with the following property*:

Let the sequence of positive integers ξ *have the property that*

$$\sum_{\substack{\xi \leqslant x \\ \xi \equiv f \pmod{w}}} 1 >> x^{1-\epsilon}$$

for every positive ϵ. *Then every large* $N \equiv (2f + 1) \pmod{w}$ *is expressible in the form*

$$(x_1^n + x_2^n + \cdots + x_{n+2}^n) + (\xi_1 + \xi_2)$$

where ξ_1 *and* ξ_2 *are numbers of the "* ξ *sequence" and the* x's *are integers* $\geqslant 0$.

The following special case is of interest:

Let the ξ sequence consist of the primes $\equiv 1 \pmod{w}$ not exceeding x. Then the property $\sum_{\substack{\xi \leqslant x \\ \xi \equiv 1 \,(w)}} 1 >> x^{1-\epsilon}$ is true and hence (here $f = 1$):

Theorem III. There exists a number w *depending only on* n *such that every large* $N \equiv 3 \pmod{w}$ *is expressible in the form*

$$(x_1^n + x_2^n + \cdots + x_{n+2}^n) + (p_1 + p_2)$$

where the x's *are integers* $\geqslant 0$ *and* p_1, p_2 *are primes.*

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* Hypothesis P is that $H_{n,n}(x) >> x^{1-\epsilon}$ for any $\epsilon > 0$. Here $H_{n,n}(x)$ denotes the number of numbers $\leqslant x$ which can be expressed as a sum of n "nth powers" $\geqslant 0$. See the first part of this paper: *Proc. Ind. Acad. Sci.*, (A), 1935, **2**, 562-573.

THE RAMAN SPECTRA OF SOME ORGANIC LIQUIDS UNDER HIGH DISPERSION AND RESOLVING POWER.

(Benzene, Toluene, Phenol, Chlorobenzene, Pyridine and Cyclohexane.)

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction.*

The use of spectrographs of high dispersion and resolving power in the study of Raman spectra is obviously of great interest and importance from the point of view of the elucidation of the fine structure of some of the lines appearing in them, and the precision measurement of their wave-numbers. The chief difficulty in all such work is of course the extremely long duration of exposure required to get well-exposed photographs. Although this difficulty can be overcome to a certain extent by the use of high speed photographic plates and intense sources of illumination, the proper choice of the spectrograph is also an important matter for consideration. A new spectrograph which has been recently added to the Physics Laboratory of the Institute was found to be particularly suited for this type of work. It was therefore thought worth while to examine the Raman spectra of a few substances with this instrument.

2. *Experimental.*

The spectrograph was of Littrow model with glass optical parts, and was supplied by the firm of Adam Hilger Ltd. The prisms (one 60° and the other 30°) were of large size giving a resolving power of about 3 $cm.^{-1}$ in the region between λ 4046 and λ 4358. The dispersion in the region λ 4358 was about 10 Å/mm. The instrument combined fairly good light gathering power with a high degree of optical perfection.

The experimental technique was the same as that described by the author on a previous occasion,[1] the quartz mercury arc being put in direct contact with a water mantle enveloping the Raman tube with concave metallic reflectors above and below. The slit width in all experiments was 50 μ as it was found that further diminution of it failed to bring out any additional spectral details (so far as the present work was concerned), and resulted only

[1] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 452.

in a general loss of intensity necessitating longer exposures. The illumination was so powerful, and the experimental conditions so good that a very intense spectrum of benzene could be obtained in 24 hours. Longer exposures did not reveal any additional features. Ilford golden isozenith plates with special backing were employed for photographing the spectra ; an iron arc comparison spectrum was photographed at the centre of the Raman spectrum on all the plates.

3. *Results.*

The plates were measured on a Hilger Cross-slide micrometer and the frequency shifts of the Raman lines were determined using linear interpolation from the nearest iron arc lines. In the case of sharp lines the results are correct to ± 1 cm.$^{-1}$ The 992 line of benzene and its satellites were measured several times with the greatest care, and the results in this case are probably correct to $\pm$ 0.5 cm.$^{-1}$. The complete classification of the spectra of the substances studied in the interval between λ 4046 and λ 5100 is given at the end of the paper. (Tables I to VI.)

(1) *Benzene.*—The Raman spectrum of this substance has formed the subject of investigation by several workers from diverse standpoints. The complete literature on the subject would be too lengthy, and reference may be made to Sirkar's bibliography of the Raman effect.[2] We may mention in particular the careful work of Dr. Krishnamurti,[3] and the more recent and elaborate investigation of Grassmann and Weiler.[4] The latter authors have reported many new lines of feeble intensity, all of which, however, could not be confirmed in the present work, probably because of the lack of sensitivity of the plates employed in the spectral regions concerned. In Table VII we have given our results side by side with those of the above-mentioned authors. The infra-red absorption frequencies in the last column are taken from Coblentz's book. A surprisingly close coincidence is noticed between the Raman and infra-red frequencies, but whether this coincidence is one of principle or merely accidental is a disputed point.

Placzek[5] has pointed out that the interpretation of the benzene spectrum is confronted with great difficulties. If we take the plane regular hexagonal model of the benzene molecule, then it follows from symmetry considerations that all Raman frequencies should be inactive in the infra-red and *vice versa*.

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[2] S. C. Sirkar, *Ind. Jour. Phys.*, 1932, **7**, 431; S. C. Sirkar and D. Chakravarty, *Ind. Jour. Phys.*, 1935, **9**, 553.

[3] P. Krishnamurti, *Ind. Jour. Phys.*, 1931, **6**, 543.

[4] P. Grassmann and J. Weiler, *Z. f. Phys.*, 1933, **86**, 321.

[5] G. Placzek, *Leipziger Vorträge*, 1931, S 71.

E. B. Wilson,[6] however, has expressed the view that in so far as infra-red data are lacking in precision, the coincidence of Raman and infra-red frequencies cannot be asserted with certainty "to establish a result contrary to all other evidence".

The normal vibrations of the benzene molecule have been worked out by E. B. Wilson[7] who has ascribed to it twenty distinct fundamental frequencies. Of these, seven are Raman-active, four infra-red-active, while the nine remaining fundamentals are completely inactive. Wilson's assignment of the fundamental frequencies[8] is as given below :—

Raman-active		Infra-red-active
ν_1=991 cm.$^{-1}$	ν_7=3047	ν_{11}=1040 cm.$^{-1}$
ν_2=3060	ν_8=(1584–1605)	ν_{18}=660
ν_6=605	ν_9=849	ν_{19}=1480
	ν_{10}=1178	ν_{20}=3080

"The remaining lines and bands which are nearly all much weaker than those assigned to fundamentals are to be considered as overtones and combinations from this viewpoint." It might be remarked that the classification does not account for the strong infra-red absorption frequency at 1183 whose coincidence with the Raman frequency 1178 has been pointed out by Dr. Placzek[9] as a result incompatible with the usually accepted plane model of the benzene ring with a centre of symmetry. Similarly, the origin of the Raman line at 2949 cm.$^{-1}$ which is perhaps stronger than the line at 1178 is also not quite clear. As has been pointed out by Grassmann and Weiler,[10] it might probably be the octave of the strong infra-red absorption frequency 1480. The strange coincidence of the Raman frequency 2949 of benzene with the C-H frequency observed in the case of aliphatics, as well as its disappearance in the monosubstituted benzene derivatives, has, however, been a great puzzle.[11]

[6] E. B. Wilson, *Phys. Rev.*, 1934, **46**, 146.

[7] E. B. Wilson, *Phys. Rev.*, 1934, **45**, 706.

[8] E. B. Wilson, *Phys. Rev.*, 1934, **46**, 146.

[9] G. Placzek, *Quantenmechanik der Materie und Strahlung*, Teil II, S 235.

[10] P. Grassmann and J. Weiler, *Loc. cit.*

[11] See K. W. F. Kohlrausch, *Der Smekal-Raman Effekt*, p. 225.

According to Wilson,[12] the doublet at 1600 cm.$^{-1}$ in the Raman spectrum of benzene is to be explained on the basis of quantum-mechanical resonance (as in the case of CCl_4) because the sum $\nu_1+\nu_6 = 1596$ cm.$^{-1}$ falls between the members of the doublet ν_8. He has also pointed out that additional evidence in support of this view is provided by the Raman spectra of benzene derivatives. "In nearly all of these a single line occurs near 1600 cm.$^{-1}$; *in none of them is a doublet reported.* This is in harmony with the fact that the accidental degeneracy $\nu_1+\nu_6 \sim \nu_8$ is not nearly so close as in benzene." The above statement appears to have been made from an insufficient knowledge of the experimental data. To illustrate this point, we give below the following table :—

Substance	Frequencies and relative intensities		
C_6H_6	606 (5)	992·5 (10)	1584 (3), 1605 (2)
$C_6H_5CH_3$	622 (4*b*)	1005 (10*s*)	1588 (2), 1606 (3), 1630 (0)
C_6H_5Cl	615 (3)	1003 (10*s*)	1565 (0), 1584 (4)
C_6H_5OH	620 (4)	1001 (10)	1595 (5), 1605 (5)
C_5H_5N	602 (1)	990 (10)	1570 (2), 1579 (2), 1594 (1)

The structure of the benzene molecule has been the theme of a recent note in *Nature* by Angus, Bailey, Ingold, Leckie, Raisin, Thompson and Wilson[13] who have investigated the Raman and infra-red spectra of hexa-deutero-benzene. Coincident frequencies are found in this case also, though not so many as in the case of benzene. These authors therefore believe that these are not coincidences of principle, but are accidental, and come to the conclusion that no real objection remains against the usually accepted structure of the benzene molecule.

Further discussion of the Raman spectrum of benzene is postponed to the next section.

(2) *Toluene.*—The Raman spectrum of this substance has been studied under high dispersion by Howlett[14] and also by Mesnage.[15] More recently,

[12] E. B. Wilson, *Phys. Rev.*, 1934, **46**, 146.

[13] W. R. Angus, C. R. Bailey, C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson and C. L. Wilson, *Nature*, 1935, **136**, 680.

[14] L. E. Howlett, *Canad. Jour. Res.*, 1931, **5**, 572.

[15] P. L. Mesnage, *Jour. de Phys.*, 1931, **2**, 403.

Kohlrausch[16] has made a systematic reinvestigation of the Raman spectra of benzene derivatives. The Raman frequencies are given in Table VIII. The infra-red absorption maxima are given in the last column. Here again, we find many frequencies common to the Raman and infra-red absorption spectra. A number of new Raman lines have been found in the region between $\Delta\nu = 1200$ and 1500 cm.$^{-1}$, some of which correspond to the infra-red frequencies present in this interval.

(3) *Phenol.*—The Raman frequencies of this substance obtained in the present investigation are given along with those reported by Kohlrausch[17] in Table IX. Several new frequencies have been found, and some of the lines previously reported as broad have been found to be doublets: *e.g.*, 1162 (5*b*), 1599 (7*b*), and 3060 (12*b*). The broad diffuse band at 3524 cm.$^{-1}$, also reported by Kohlrausch is to be attributed to the O–H oscillation.

(4) *Chlorobenzene.*—Murray and Andrews[18] have made a detailed study of the Raman spectrum of C_6H_5Cl and have reported several new lines. Many of these are confirmed by the present work. The Raman frequencies and infra-red absorption maxima are given in Table X.

(5) *Pyridine.*—Krishnamurti[19] has made a detailed study of the Raman spectrum of pyridine and has reported several new frequencies. Very recently Kohlrausch and Pongratz[20] have studied the Raman spectrum of this substance. Unfortunately, the latter authors have overlooked the work of Krishnamurti, so that not only those frequencies which they report as new, but several other frequencies not obtained by them are contained in Krishnamurti's paper. The present work confirms almost all the frequencies reported by Krishnamurti and also shows that some of these frequencies are actually doublets. The results are given in Table XI. The remarkable coincidence between the Raman and infra-red absorption frequencies may be seen from the table.

(6) *Cyclohexane.*—A careful investigation of the Raman spectrum of this substance has been made by Krishnamurti[21] whose results along with those of the author are given in Table XII. The line $\Delta\nu = 992$ (0) arises most probably from a trace of benzene impurity. The line $\Delta\nu = 695$ (0) reported by Krishnamurti is not confirmed as the corresponding line is not

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[16] K. W. F. Kohlrausch and A. Pongratz, *Sitz. der Kais. Acad. Wiss.*, 1933, **142**, 637.

[17] K. W. F. Kohlrausch and A. Pongratz, *Loc. cit.*

[18] J. M. Murray and D. H. Andrews, *Jour. Chem. Phys.*, 1933, **1**, 402.

[19] P. Krishnamurti, *Ind. Jour. Phys.*, 1931, **6**, 543.

[20] K. W. F. Kohlrausch and A. Pongratz, *Ber. der Deut. Chem. Gess.*, 1934, **67**, 1465.

[21] P. Krishnamurti, *Ind. Jour. Phys.*, 1931, **6**, 543.

observed by 4046 excitation. It would seem that the line in question is really the 802 line excited by λ 4339 and not 695 coming from λ 4358. Between $\Delta\nu = 2852$ 2922 cm.$^{-1}$ Krishnamurti has reported a continuous background and a line at 2889. In the present work three lines 2870, 2888 and 2898 are observed in this region.

4. The Carbon Isotope and the Fine Structure of the 992 *Line of Benzene.*

The fine structure of the Raman line 992 cm.$^{-1}$ of benzene has been investigated by Weiler,[22] Howlett,[23] Mesnage,[24] L. and E. Bloch,[25] Grassmann and Weiler,[26] Specchia and Scandurra[27] and more recently by Bhagavantam.[28] The following table gives a collective summary of the results of various investigators :—

Author	Frequencies and Relative Intensities				
J. Weiler (1931) ..	982 (1)		992·0 (4)		
L. E. Howlett (1931) ..	980·3 (5)	983·9 (5)	992·2 (10)	998·5 (5)	1005·3 (0)
P. L. Mesnage (1931) ..	981·2 (2)		992·4 (10)		
L. and E. Bloch (1933) ..	978·5 (0)	983·8 (2)	992·2 (20)	999·0 (1)	1006·0 (0)
P. Grassmann and J. Weiler (1933) ..	979 (1)	984 (2)	992·5 (15)	(999)	1005 (1)
O. Specchia and G. Scandurra (1935) ..	977	984	992	1002	
S. Bhagavantam (1935) ..		985 (1)	992·2 (20)		
R. Ananthakrishnan (1935)	979 (½)	984(1)	992·5 (10)	998 (1)	1006 (½)

A little consideration will show that the results of the different workers are not really discordant except in so far as the visual estimates of the relative intensities are concerned. The latter remark applies especially to

[22] J. Weiler, *Z. f. Phys.*, 1931, **69**, 586.

[23] L. E. Howlett, *Loc. cit.*

[24] P. L. Mesnage, *Loc. cit.*

[25] L. and E. Bloch, *C.R.*, 1933, **196**, 1787.

[26] P. Grassmann and J. Weiler, *Loc. cit.*

[27] O. Specchia and G. Scandurra, *N. Cimento*, 1935, **12**, 129.

[28] S. Bhagavantam, *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 86.

Howlett's intensity estimates of the satellites which are certainly far too high. As regards the frequencies themselves, it might be pointed out that 982 and 981·2 reported by Weiler and Mesnage respectively may be regarded as the mean of the two frequencies 979 and 984, the separation being not observed by them, probably on account of the insufficient resolving power of the instruments employed. The 1002 lines reported by Specchia and Scandurra is perhaps the mean of 998 and 1006. The line at 998 cm.$^{-1}$ is just resolved from the main line at 992·5 and appears as a wing to the latter. Such a wing to the total symmetric vibration Raman line of CCl_4 has been recently reported by the author.[29] A microphotometric study of the intensity distribution in the wing in these two cases would appear to be of great interest in view of the recent work of Bhagavantam, Weiler and others on the distribution of intensity in the rotational wings accompanying the Rayleigh line in the case of liquids.

The author's findings regarding the fine structure of the 992 line of benzene stands in good agreement with that of Grassmann and Weiler, L. E. Howlett and L. and E. Bloch. In view of this, the remark of Bhagavantam[30] that "the failure to record the other components, *viz.*, 980·3, 999, etc., in the present investigation is very significant..... A possible explanation is that they have arisen from traces of impurities such as toluene, etc., ..." does not seem to be justified. The fact that Bhagavantam could record only the strongest satellite was probably because either the duration of exposure or the resolving power of the instrument employed was insufficient.

As is well known, the Raman line 992·5 cm.$^{-1}$ in the case of benzene, corresponds to the symmetrical expansion and contraction of the benzene ring. Following the original suggestion of Gerlach,[31] Grassmann and Weiler, Specchia and Scandurra, and Bhagavantam have attributed the strong satellite at 984 cm.$^{-1}$ to the vibration of the benzene nucleus in which one of the six carbon atoms is the heavier isotope C_{13}. The satellites of lesser intensity are, in the opinion of Grassmann and Weiler, to be interpreted as combinational tones. In order to investigate the matter more thoroughly, these authors undertook polarisation measurements and found that the satellite at 984 is polarised to the same extent as the principal line at 992·5. However, they were unable to draw any conclusions as regards the state of polarisation of the other satellites since these could not be recorded in the polarisation experiments on account of their feeble intensity.

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29 R. Ananthakrishnan, *Loc. cit.*

30 S. Bhagavantam, *Loc. cit.*

31 W. Gerlach, *Ber. d. Bayr. Akad. d. Wiss.*, 1932, 1, 39.

Following Bhagavantam, we can calculate to a first order of approximation the change in frequency that would be produced if one of the six carbon atoms of the benzene nucleus were to be replaced by the isotope C_{13}. If the symmetrical expansion of the benzene ring C_6^{12} has got the frequency 992·5, the corresponding frequency for the ring $C_5^{12}C^{13}$ works out easily as 986, provided it be assumed that the introduction of the heavier isotope does not appreciably affect the symmetry character of the ring. The deviation between the observed frequency 984 and the calculated frequency 986 appears to be too great to attribute it to an error in measurement.

The abundance ratio of the carbon isotopes C^{12} and C^{13} as given by different workers is very divergent. The recent estimate of Aston[32] gives the most probable value ratio of abundance as $C^{13} : C^{12} :: 1 : (140 \pm 14)$. As Bhagavantam has pointed out, this ratio gives for the expected satellite an intensity which is roughly 1/23rd of the intensity of the main line. Although too much emphasis cannot be laid on visual estimates of intensity, it appears from the photographs that the relative intensity of the satellite at 984 is greater than this value.

We shall now consider a little more closely the Raman spectra of the monosubstituted derivatives of benzene. It is well known that a number of the Raman lines of benzene occur also in its monoderivatives with practically the same frequency and degree of depolarisation. These frequencies have therefore their origin presumably in the vibrations of the carbon ring. In the case of benzene these frequencies have the following values :

$\Delta\nu = 606$, 992, 1176, 1600 (double) and 3060 (double). Of these $\Delta\nu = 992$ cm.$^{-1}$ is of special interest for reasons already pointed out. In the monoderivatives of benzene the corresponding line has a slightly higher

Substance	Frequency and Relative Intensities								
C_6H_6	979 ($\frac{1}{2}$)	984 (1)		992·5 (10)	998 (1) (wing)		1006 ($\frac{1}{2}$)		
$C_6H_5CH_3$	978 ($\frac{1}{2}$)			993 ($\frac{1}{2}$)			1005 (10)		
C_6H_5Cl		989 (0)			1003 (1)			1013 (00)	
C_6H_5OH		991 (00)			1001 (10)			1013 (0) (wing)	
C_5H_5N	979 (0)	990 (10)							

[32] F. W. Aston, *Proc. Roy. Soc.*, A, 1935, **149**, 396.

frequency, and the present investigation shows that in all cases it is accompanied by faint satellites.

The faint companion to the shorter wave-length side of the strong line is in all cases very sharp but its frequency and relative intensity do not seem to bear any simple relation to those of the main line. Its relative intensity is greatest in the case of toluene and least in the case of phenol.

Structure of the Raman line 802 *cm.*$^{-1}$ *of cyclohexane.*—As in the case of the 992·5 line of benzene, the 802 line of cyclohexane represents the frequency of the symmetric expansion and contraction of the puckered carbon ring which forms the nucleus of this molecule. Bhagavantam[33] has reported an "unresolved blackening" to the shorter wave-length side of this line, which, however, is not confirmed by the present work. It seems desirable to point out the remarkable dissimilarity in the structure of the Raman line corresponding to the symmetrical vibration in the case of benzene and cyclohexane. An enlargement of these two lines excited by λ 4047 is reproduced in the Plate. The 802 line of cyclohexane is quite sharp and is completely free from wings and satellites. If the satellite at 984 cm.$^{-1}$ in the case of benzene is to be attributed to the nucleus $C_5^{12}C^{13}$, we ought to expect a similar satellite with the same relative intensity and a frequency shift of 796·7 cm.$^{-1}$ in the case of cyclohexane. The fact that there is not even the faintest trace of such a satellite, when taken together with other difficulties already pointed out, renders it highly improbable that the 984 satellite of benzene has its origin in the carbon isotope.

5. *Conclusion.*

The present investigation shows that there exists a fundamental difference between the structure of the 992 line of benzene and the corresponding line in the case of its monosubstituted derivatives. How far it is correct to interpret the satellites of the 992·5 line of benzene as well as many of the less intense lines in its Raman spectrum as over- and combinational tones remains an open question. That the benzene problem is beset with several difficulties has been already emphasised. It may be that many of these difficulties as well as the fine structure of the 992 line itself are all intimately connected with the constitution of the benzene ring which is still a problem not completely understood.

The author wishes to express his respectful thanks to Professor Sir C. V. Raman for his kind interest and suggestions in the course of the present work.

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[33] S. Bhagavantam, *Loc. cit.*

Summary.

A detailed study of the Raman spectra of benzene, toluene, phenol, chlorobenzene, pyridine and cyclohexane has been made with a spectrograph of high dispersion and resolving power. Several faint lines have been observed in the Raman spectra of these substances many of which agree with those reported by previous workers, and some of which are reported for the first time. The Raman spectrum of phenol in particular shows several new features. A careful study has been made of the fine structure of the 992 line of benzene, and it is found to consist of four satellites in addition to the main line at 992·5 cm.$^{-1}$ The frequencies and relative intensities are: 979 ($\frac{1}{2}$), 984 (1), 992·5 (10), 998 (1), 1006 ($\frac{1}{2}$). The corresponding Raman line (802 cm.$^{-1}$) in the case of cyclohexane shows no fine structure. The possibility of the 984 satellite of benzene arising from the carbon isotope C^{13} has been discussed, and several difficulties are pointed out which render it difficult to attribute such an origin to this satellite. The study of the Raman spectrum of the monoderivatives as well as of pyridine shows that the intense Raman line which corresponds to the symmetrical expansion and contraction of the nucleus is in all cases accompanied by a faint companion to the shorter wave-length side. The frequency and relative intensity of this satellite, however, seem to bear no unique relation to those of the main line. It is concluded that the peculiar structure of the 992 line of benzene is probably connected with the constitution of the benzene ring.

Note on chemicals.—The benzene employed in the present work was the " Kahlbaum " variety for the determination of molecular weight. No special purification was therefore considered necessary excepting the usual process of vacuum distillation to remove suspended motes. Toluene, pyridine and chlorobenzene were subjected to preliminary fractionation in a rectifying column, and the middle fractions distilling at constant boiling point were used in the experiment. Phenol was available in the pure crystalline state, while cyclohexane was taken from a bottle labelled " pure " and supplied by the firm of Theodor Schucardt.

The duration of exposure varied from 24 hours in the case of benzene and chlorobenzene to 48 hours in the case of toluene, pyridine and phenol. Cyclohexane gave a very clear and intense Raman spectrum with a continuous exposure of 80 hours. It may be interesting to add that phenol was a supercooled liquid at 25°C. during the time of exposure.

The notation employed in the accompanying Tables is as follows and is taken from Kohlrausch's well-known book :—

Exciting line Å	Notation	Wave Number (cm.$^{-1}$)
4358·34	*e*	22938
4347·50	*f*	22995
4339·24	*g*	23039
4108	*h*	24335
4077·84	*i*	24516
4046·56	*k*	24705·4
3984	*l*	25098
3906	*m*	25592
3663	*o*	27293
3655	*p*	27353
3650	*q*	27388

Diffuse lines of zero intensity whose assignments are not quite certain are indicated by an interrogation mark. An asterisk against some of the frequencies indicates that the corresponding lines show a doublet structure.

The abbreviations employed in the Tables have the following significance :—

s = sharp ; b = broad ; d = diffuse ; vb = very broad.

Anti-stokes lines are indicated by a bar placed over the corresponding frequencies.

TABLE I. *Raman Spectrum of Benzene.*

No.	ν	Int.	Assignment	No.	ν	Int.	Assignment
1	19874	3	*e*—3064	37	22535	1*d*	*e*—403 *m*—3057
2	19890	1	*e*—3048	38	23100	2	*k*—1605
3	19988	0	*e*—2950	39	23121	3	*k*—1584
4	21333	2	*e*—1605 *i*—3188	40	23230	0	*k*—1475
				41	23260	0	*k*—1445
5	21353	3	*e*—1585 *i*—3167	42	23302	½*d*	*k*—1403
6	21392	0	*f*—1603	43	23341	1*d*	*h*—992 *i*—1175
7	21412	0	*f*—1583	44	23383	0*d*	*o*—3910?
8	21454	3	*e*—1484 *i*—3062	45	23435	0*d*	*p*—3918?
				46	23480	0*d*	*q*—3908?
9	21468	½	*i*—3041	47	23523·5	6	*i*—992·5
10	21493	00	*e*—1445	48	23532	2	*i*—984 *k*—1173
11	21518	1	*k*—3187				
12	21541	½	*e*—1397 *k*—3164	49	23544	½	*e*—606
13	21566	½	*i*—2950	50	23670	½	*i*—846 *k*—1035
14	21589	00	*i*—2927	51	23699·4	½	*k*—1006
15	21642	8	*k*—3063	52	23707·6	2	*k*—997·8
16	21657	4	*k*—3048	53	23712·6	15	*k*—992·8
17	21756	5	*k*—2949	54	23721·4	2	*k*—984
18	21762	2	*e*—1176	55	23726	1	*k*—979·4
19	21777	0*bd*	*k*—2928	56	23855	1*d*	*k*—850
20	21820	0	*f*—1175	57	23905	½	*k*—800
21	21862	00	*g*—1177	58	23930	1	*e*—992 *k*—775
22	21904	0	*e*—1034				
23	21933	0	*e*—1005	59	24009	00*d*	*k*—686
24	21945·2	10	*e*—992·8	60	24099	5*b*	*k*—606 *o*—3194
25	21954	1	*e*—984				
26	21959	0	*e*—979	61	24125	1*d*	*o*—3168
27	22003·5	3	*f*—991·8	62	24165	2	*p*—3188
28	22047	2	*g*—992	63	24185	0	*p*—3168
29	22088*	2	*e*—850 *k*—2617	64	24201	4	*q*—3187
				65	24228	6*b*	*o*—3065 *q*—3160
30	22136	0	*e*—802	66	24242	1	*o*—3051
31	22158	½	*e*—780 *k*—2547	67	24286	8	*p*—3067
32	22248*	½	*e*—690 *k*—2457	68	24305	1	*k*—400 *p*—3048
33	22331	5	*e*—607	69	24325	9	*q*—3063
34	22388	0	*f*—607	70	24344	4*d*	*o*—2949
35	22413	0	*k*—2292	71	24404	3	*p*—2949
36	22438	0	*g*—601	72	24438	5	*q*—2950

402(1*d*), 606(5), 688(½), 778(0), 801(0), 850(2), 979(½), 984(1), 992·5(10), 998(1), 1006(½), 1035(0), 1175(2), 1400(½), 1445(0), 1480(0), 1584(3), 1605(2), 2292(0), 2457(½), 2547(½), 2617(0), 2928(0*d*), 2949(5), 3048(4), 3064(8), 3164(½), 3187(1), (3910)(0*d*).

TABLE II.

Raman Spectrum of Toluene.

No.	ν	Int.	Assignment	No.	ν	Int.	Assignment
1	19980	3*b*	*e*—3058	46	23206	0	*k*—1499
2	20018	2	*e*—2920	47	23250	0*d*	*k*—1455
3	21315	0	*e*—1623	48	23272	0*d*	*k*—1433
4	21331	3	*e*—1607	49	23304	1*s*	*i*—1213 *k*—1401
5	21350	2	*e*—1588				
6	21387	00	*f*—1608	50	23324	3	*k*—1381
7	21406	00	*f*—1599	51	23357	0*d*	*i*—1159
8	21460	2*b*	*i*—3056	52	23390	0*d*	*k*—1315
9	21484	0	*e*—1454	53	23423	0*d*	*k*—1282
10	21503	0	*e*—1435	54	23457	1	*e*—519
11	21534	½*s*	*e*—1404	55	23485	1	*i*—1031
12	21555	2*s*	*e*—1383	56	23494	6*s*	*k*—1211
13	21597	½*b*	*i*—2919	57	23510	4*s*	*i*—1006
14	21634	6*b*	*k*—3071	58	23524	1	*k*—1181
15	21645	8	*k*—3060	59	23548	2	*k*—1157
16	21668	4*b*	*k*—3037	60	23672	8*s*	*k*—1033
17	21703	½	*k*—3002	61	23699	10*s*	*k*—1006
18	21725	6*s*	*e*—1213	62	23711	½*s*	*k*—993
19	21756	1	*e*—1182	63	23722	0	*e*—784
20	21783	6*b*	*e*—1155 *k*—2922	64	23728	1	*i*—788 *k*—977
21	21837	3*vb*	*k*—2868	65	23811	0*b*	*k*—894
22	21909	8*s*	*e*—1029	66	23865	0*b*	*k*—840
23	21933	10*s*	*e*—1005	67	23895	0*b*	*i*—621 *k*—810
24	21945	½*s*	*e*—993				
25	21960	½	*e*—978	68	23917	10*s*	*k*—788
26	21968	0	*f*—1027	69	23941	0	*e*—1003
27	21989	½*s*	*f*—1006	70	23969	0	*e*—1031
28	22009	00	*g*—1030	71	23975	0	*k*—730
29	22034	0	*g*—1005	72	23993	½*s*	*i*—523
30	22040	0*b*	*e*—898	73	24084	4*b*	*k*—621
31	22095	0*b*	*e*—843	74	24124	0*b*	*k*—581?
32	22122	0*b*	*e*—816	75	24182	6*s*	*k*—523
33	22150	9*s*	*e*—788	76	24220	3	*o*—3073
34	22205	½	*e*—733 *f*—790	77	24234	6	*o*—3059
				78	24255	1*d*	*o*—3038
35	22250	0	*g*—789	79	24284	4	*p*—3069
36	22314	3	*e*—624	80	24296	6	*p*—3057
37	22415	5	*e*—523	81	24139	5*b*	*q*—3069 *o*—3034
38	22470	½	*f*—525				
39	22537	0*vb*	*m*—3055	82	24350	4*b*	*q*—3038 *p*—3003
40	22604	½	*e*—334				
41	22670	0	*m*—2922	83	24370	4*b*	*o*—2933
42	22720	6*b*	*e*—218	84	24382	½	*q*—3006
43	23099	3	*k*—1606	85	24429	6*b*	*p*—2924
44	23118	1	*k*—1587	86	24465	6*b*	*q*—2933
45	23153	1*b*	*e*—215				

216 (6*b*), 334 (½), 523 (5), (581) (0), 622 (4*b*), 730 (0), 788 (10), 813 (0*b*), 842 (0*b*), 896 (0*b*), 978 (½), 993 (½), 1005 (10*s*), 1030 (8*s*), 1157 (2), 1181 (1), 1212 (6*s*), 1282 (0), 1315 (0), 1348 (0), 1381 (2), 1402 (0), 1434 (0), 1455 (0), 1499 (0), 1588 (2), 1606 (3), 1630 (0), 2868 (3*vb*), 2922 (6*b*), 3002 (½), 3037 (4*b*), 3058 (8), 3070 (6*b*).

TABLE III.

Raman Spectrum of Phenol.

No.	ν	Int.	Assignment	No.	ν	Int.	Assignment
1	19879	3*b*	*e*—3059	40	22530	0*bd*	*m*—3062
2	21171	0*bd*	*k*—3524	41	22696	5*b*	*e*—242
3	21332	5	*e*—1606	42	23100	5	*k*—1605
4	21342	5	*e*—1596	43	23111	5	*k*—1594
5	21394*	00*b*	*f*—1601	44	23179	2*b*	*e*—241
6	21441	½	*e*—1497	45	23206	0	*k*—1499
7	21455	2*b*	*i*—3061	46	23241	0	*k*—1464
8	21505*	0*bd*	*k*—3200	47	23280	00	*k*—1425
9	21555	00*d*	*k*—3150	48	23345	0	*i*—1171
10	21620*	½ (*wing*)	*k*—3085	49	23360	0	*i*—1156
				50	23449	2*b*	*k*—1256
11	21641	8	*k*—3064	51	23473	0	*e*—535
12	21654	5	*k*—3051	52	23490	1	*i*—1026
13	21688	2*b*	*e*—1250	53	23515	3	*i*—1001
14	21714	½*b*	*k*—3017	54	23535	3	*k*—1170
15	21740	00*b*	*f*—1255	55	23550	3	*k*—1155
16	21768	4*s*	*e*—1170	56	23592	0	*k*—1113
17	21784	3*s*	*e*—1154	57	23634	1	*k*—1071
18	21825	0	*e*—1113? *f*—1170	58	23678	8	*k*—1027
19	21840	00	*f*—1155	59	23693	0 (*wing*)	*e*—755 *k*—1012
20	21866	1*s*	*e*—1072				
21	21911	8*s*	*e*—1027	60	23704	10	*k*—1001
22	21923	0 (*wing*)	*e*—1015	61	23715	00	*k*—990
				62	23754	0	*e*—816
23	21937	10	*e*—1001	63	23766	00	*i*—750
24	21947	00	*e*—991	64	23830	0*bd*	*p*—3520
25	21968	0	*f*—1027	65	23877	3	*i*—623 *k*—828
26	21994	½*s*	*f*—1001				
27	22040	0	*g*—999	66	23893	8	*k*—812
28	22107	4	*e*—831	67	23918	0*b*	*k*—787
29	22125	8	*e*—813	68	23950	2*b*	*k*—755
30	22153	0*d*	*e*—785	69	23982	½	*i*—534
31	22181	3*b*	*e*—757 *f*—814	70	24000	00*d*	*k*—705
				71	24085	4	*k*—620
32	22227	00*d*	*g*—812	72	24114	0*d*	*k*—591
33	22273	00*d*	*e*—665	73	24171	4*b*	*k*—534
34	22319	5*s*	*e*—619	74	24199	½	*k*—506
35	22349	00	*e*—589	75	24230	4*b*	*o*—3063
36	22377	00	*f*—618	76	24270	½	*i*—246
37	22407	4	*e*—531	77	24289	6*b*	*p*—3062
38	22430	1	*e*—508	78	24324	6	*q*—3064
39	22460	0	*f*—530	79	24462	4*b*	*k*—243

243 (5*b*), 507 (½), 532 (4), 590 (0), 620 (4), 655 (00*d*), 756 (3), 787 (0*b*), 812 (8), 830 (3), 991 (0), 1001 (10), 1013 (0), 1027 (8*s*), 1072 (1), (1113) (0), 1155 (3*s*), 1170 (4*s*), 1253 (2*b*), (1425) (00), 1464 (0), 1498 (½), 1595 (5), 1605 (5), 3017 (½*b*), 3051 (5), 3064 (8), 3035 (½) (3150) (00*d*), 3200 (0*bd*), 3524 (0*vb*).

TABLE IV.

Raman Spectrum of Chlorobenzene.

No.	ν	Int.	Assignment	No.	ν	Int.	Assignment
1	19870	2*b*	*e*—3066	38	23336	0	*k*—1369
2	21353	3	*e*—1585	39	23358	1	*e*—$\overline{4^{-}0}$
3	21373	0	*e*—1565	40	23384	0	*k*—1321
4	21413	00	*f*—1582	41	23410	0	*k*—1295 ?
5	21448	2	*i*—3068	42	23435	½	*i*—1081
6	21492	0	*e*—1446	43	23493	1*s*	*i*—1023
7	21542	1	*k*—3163	44	23514	2*s*	*i*—1002
8	21564	0	*e*—1374 *k*—3141	45	23531	½	*k*—1174
				46	23548	1	*k*—1157
9	21616	0	*e*—1322	47	23585	½	*k*—1120
10	21637	10*b*	*k*—3068	48	23622	5	*k*—1083
11	21677	0	*k*—3028	49	23638	0	*e*—700
12	21697	0	*k*—3008	50	23681	8	*k*—1024
13	21760	0	*e*—1178	51	23692	00	*k*—1013
14	21780	½	*e*—1158	52	23702	10*s*	*k*—1003
15	21815	0	*e*—1123	53	23715	0*s*	*k*—990
16	21853	4	*e*—1085	54	23780	0	*k*—925
17	21914	6*s*	*e*—1024	55	23815	½	*i*—701
18	21925	00	*e*—1013	56	23874	0	*k*—831
19	21935	10*s*	*e*—1003	57	23904	0	*i*—612
20	21949	0*s*	*e*—989	58	23917	00	*k*—788
21	21971	0*s*	*f*—1024	59	23941	0*s*	*e*—$\overline{1003}$
22	21993	½*s*	*f*—$\overline{1012}$	60	23961	0	*e*—$\overline{1023}$ *k*—744
23	22015	00	*g*—1024				
24	22037	0	*g*—1002	61	24002	6	*k*—702
25	22108	0	*e*—830	62	24090	3	*k*—615
26	22148	00	*e*—790	63	24127	0	*o*—3166
27	22198	0	*e*—740	64	24193	0	*p*—3160
28	22236	5*s*	*e*—702	65	24223	6*b*	*o*—3070
29	22295	0	*f*—700	66	24264	0	*o*—3029
30	22335	3	*e*—615	67	42284	10*b*	*k*—421 *p*—3069
31	22518	6	*e*—420				
32	22643	3	*e*—295	68	24318	10	*q*—3070
33	22742	6*b*	*e*—196	69	24364	½*d*	*q*—3021
34	23121	5	*k*—1584	70	24387	½	*q*—3001
35	23132	4	*e*—$\overline{194}$	71	24407	2	*k*—298
36	23239	½	*e*—$\overline{301}$	72	22435	½	*k*—270?
37	23265	0	*k*—1440				

196 (6*b*), (270) (½), 295 (2), 420 (6), 615 (3), 702 (6), 742 (0), 790 (0), 830 (0), (925) (0), 989 (0*s*), 1003 (10*s*), 1013 (00), 1024 (7), 1084 (5), 1121 (½), 1158 (½), 1176 (½), (1295) (0), 1321 (0), 1372 (0), 1443 (0), 1565 (0), 1584 (4), 3008 (5), 3028 (0), 3068 (10*b*), 3140 (0), 3165 (1).

TABLE V.

Raman Spectrum of Pyridine.

No.	ν	Int.	Assignment	No.	ν	Int.	Assignment
1	19884	1½	*e*—3054	32	22561	00	*e*—377 ?
2	21345	½	*e*—1593	33	23111	1	*k*—1594
3	21359	2	*e*—1579	34	23125	2	*k*—1580
4	21367	2	*e*—1571	35	23136	2	*k*—1569
5	21416*	00	*i*—1579	36	23220	1	*k*—1485
6	21461	1	*e*—3055	37	23303	0	*i*—1213
7	21494	0	*k*—1444?	38	23488*	5	*i*—1028 *k*—1217
8	21533	½	*k*—3172				
9	21563	1½	*k*—3142	39	23525	4*s*	*i*—991
10	21615	½	*k*—3090	40	23560	0*d*	*k*—1145
11	21642	½	*k*—3063	41	23591	0*d*	*e*—653
12	21652	8*b*	*k*—3053	42	23647	0	*k*—1058
13	21671	½	*k*—3034	43	23667	0	*k*—1038
14	21680	½	*k*—3025	44	23677	10*s*	*k*—1028
15	21719	3	*e*—1219 *k*—2986	45	23716	10*s*	*k*—989
				46	23726	0	*k*—979
16	21754	1	*k*—2951	47	23763	0	*k*—942
17	21797*	½*d*	*e*—1141 *k*—2908	48	23827	½	*k*—878
				49	23871	00	*i*—645
18	21834	0*d*	*k*—2871	50	23906	0	*k*—799
19	21882	0	*e*—1056	51	23930	0	*e*—992
20	21897	0	*e*—1041	52	23968	00	*e*—1030
21	21909	10*s*	*e*—1029	53	24052	3	*k*—653
22	21948	10*s*	*e*—990	54	24103	½	*k*—602
23	21959	0	*e*—979	55	24158*	0	*o*—3073
24	21966	0	*f*—1029	56	24238	5*b*	*o*—3055
25	22006	½	*f*—989	57	24265*	0	*o*—3028
26	22047*	½	*e*—891 *g*—992 *k*—2658	58	24285	0	*p*—3068
				59	24298	6*b*	*k*—407 *p*—3055
27	22256	0	*k*—2449	60	24318	0	*q*—3070
28	22286	3	*e*—652	61	24335	6*b*	*q*—3053
29	22335	1	*e*—603 *k*—2370	62	24356	0	*q*—3032
				63	24367	0	*q*—3021
30	22385	0	*e*—553?	64	24399	1	*p*—2954
31	22536	1	*e*—402	65	24436	1½	*q*—2952

(377) (0), 402 (1), (553) (0), 602 (1), 652 (3), 799 (0), 878 (½), 942 (0), 979 (0), 990 (10), 1028 (10), 1040 (0), 1057 (0), 1143 (½), 1218 (3), (1444) (0), 1485 (1), 1570 (2), 1579 (2), 1594 (1), 2370 (0), 2449 (0), (2658) (0), 2871 (0), 2908 (0), 2951 (1), 2986 (0), 3025 (½), 3034 (½), 3054 (8*b*), 3063 (½), 3090 (½), 3142 (1½) 3172 (½).

TABLE VI.

Raman Spectrum of Cyclohexane.

No.	ν	Int.	Assignment	No.	ν	Int.	Assignment
1	20001	5	*e*—2937	32	22335	0	*e*—603
2	20016	5	*e*—2922	33	22352	0	*k*—2353
3	20046	1*b*	*e*—2892	34	22512	1	*e*—426
4	20084	8	*e*—2854	35	22554	½	*e*—384
5	20238	0	*e*—2700	36	22654	½*d*	*m*—2938
6	20278	1	*e*—2660	37	22737	½	*m*—2855
7	20311	½	*e*—2627	38	22765	0	*e*—173?
8	20580	0	*e*—2358	39	22795	0	*e*—143?
9	21493	5*b*	*e*—1445	40	23072	0*b*	*i*—1444
10	21555	0*d*	*f*—1440	41	23265	5*b*	*k*—1440
11	21578	4	*i*—2938	42	23319	0*d*	*e*—$\overline{381}$
12	21591	4	*e*—1347 *i*—2925	43	23357	1	*e*—$\overline{419}$ *k*—1348
13	21662	6	*i*—2854	44	23440	5	*k*—1265
14	21672	6	*e*—1266	45	23487	1	*i*—1029
15	21768	8	*k*—2937	46	23549	3*s*	*k*—1156
16	21784	8	*e*—1154 *k*—2921	47	23676	5	*k*—1029
				48	23714	4*s*	*i*—802
17	21807	2	*k*—2928	49	24738	1*s*	*e*—$\overline{800}$
18	21817	2	*k*—2888	50	24902	10*s*	*k*—803
19	21835	1	*k*—2870	51	24107	0*b*	*k*—598?
20	21852	10	*k*—2853	52	24218	½*d*	*e*—$\overline{1280}$
21	21909	6	*e*—1029	53	24278	1	*k*—427
22	21946	0	*e*—992	54	24352	8	*o*—2941
23	21962	0	*f*—1033	55	24369	8	*o*—2924
24	22009	1	*k*—2696	56	24426	8	*p*—2927
25	22014	00	*g*—1025	57	24440	7	*o*—2853
26	22040	2	*k*—2665	58	24457	8	*q*—2931
27	22071	1*s*	*k*—2634	59	24468	8	*q*—2920
28	22100	0*d*	*k*—2605	60	24502	8	*p*—2851
29	22136	10*s*	*e*—802	61	24537	10*b*	*q*—2851
30	22192	1*s*	*f*—803	62	24591	1*d*	*o*—2702
31	22238	½*b*	*g*—801 *k*—2467 ?	63	24632	2	*o*—2661
				64	24656	2	*p*—2697

384 (½), 426 (1), (600) (0), 802 (10), 1029 (6), 1156 (3), 1265 (5), 1348 (1), 1442 (5*b*), 2353 (0), 2467 (0), 2605 (0), 2630 (1), 2662 (2), 2698 (1), 2853 (10*b*), 2870 (1), 2888 (2), 2898 (2), 2922 (8), 2937 (8).

TABLE VII.

Benzene.

Author	Krishnamurti	Grassmann and Weiler	Infra-red Absorption maxima
400 (1*d*)	407 ($\frac{1}{2}$)	404 (1*d*)	
606 (5)	603 (3)	606·8 (8)	
688 ($\frac{1}{2}$)	687 (0)	692 (1)	694
778 (0)		781 (1)	782
801 (0)	806 (0)	802 (0)	803
		824 ($\frac{1}{2}$)	820
850 (2)	848 (2)	849 (4*d*)	847
979 ($\frac{1}{2}$)	976 (0)	979 (1)	971
984 (1)		984 (2)	
992·5 (10)	992 (10)	992·5 (15*s*)	
998 (1)		(999)	
1006 ($\frac{1}{2}$)		1005 (1)	
1035 (0)	1029 (0)	1034 (1)	1025
1175 (2)	1178 (5)	1176 (4*d*)	1183
		1285 (0)	
		1326 ($\frac{1}{2}$)	1316
1400 ($\frac{1}{2}$)	1407 (0)	1403 (2)	1379
1445 (0)		1449 (0*d*)	
1480 (0)	1477 (0)	1480 (0)	1481
1584 (3)	1584 (3)	1585·4 (12)	1587
1605 (2)	1603 (2)	1606·4 (8)	1613
		1697 (0)	
		1827 ($\frac{1}{2}$)	1818
		1936 (1*d*)	
		1988 ($\frac{1}{2}$)	1968
		2030 ($\frac{1}{2}$)	2040
		2128 ($\frac{1}{2}d$)	
2272 (0)		2296 (1)	2260
		2358 ($\frac{1}{2}dd$)	2326
2457 ($\frac{1}{2}$)	2455 ($\frac{1}{2}$)	2455 (1)	
2547 ($\frac{1}{2}$)	2543 ($\frac{1}{2}$)	2545 (1)	
2617 ($\frac{1}{2}$)		2618 (2)	
		2688 ($\frac{1}{2}$)	2667
			2856
			2894
2928 (0*d*)	2928 (0)	2927 (1)	
2949 (5)	2948 (1)	2949 (4)	
3048 (4)	3046 (1)	3049 (8)	3040
3064 (8)	3063 (4)	3063·6 (12)	3074
3164 ($\frac{1}{2}$)	3164 ($\frac{1}{2}$)	3166·6 (3*s*)	
3187 (1)	3187 (1)	3187·4 (4*s*)	
		3467 (0)	
		3680 (0)	
(3910) (0)		(3916) (0)	

TABLE VIII.

Toluene.

Author	Howlett	Kohlrausch	Mesnage	Infra-red Absorption maxima
218 (6*b*)	216·7 (4)	217 (8*b*)	214·3 (*F*)	
334 ($\frac{1}{2}$)	335·0 (0)	348 (1)	341·0 (*f*)	
		405 (0)		
			461·4 (*m*)	
523 (5)	519·8 (5)	521 (7)	521·1 (*m*)	
(581) (0)				
622 (4*b*)	622·2 (3)	622 (4)	621·9 (*m*)	
730 (0)		729 (1)		725·6
788 (10)	786·7 (8)	785 (12)	785·8 (*F*)	769·3
813 (0*b*)	807·2 (0)			
842 (0*b*)	842·4 (0)	842 (1)		831·4
896 (0*b*)		892 (1)		897·1
978 (0)	968·3 (0)		977·0 (*f*)	943·4
993 ($\frac{1}{2}$*s*)	992·2 (3)		990·9 (*m*)	980·4
1005 (10*s*)	1001·9 (10)	1002 (12)	1003·8 (*F*)	
1030 (8*s*)	1027·7 (6)	1032 (6)	1027·1 (*m*)	1028
				1077
1157 (2)	1156·5 (3)	1153 (3)	1155·4 (*m*)	
1181 (1)	1180·3 (3)	1176 (1)	1178·5 (*ff*)	1170
			1187·5 (*ff*)	1191
1212 (6*s*)	1210·0 (5)	1209 (8)	1210·0 (*F*)	1234
1282 (0)			1253·7 (*f*)	1299
1315 (0)				
1348 (0)				
1381 (2)	1379·5 (2)	1377 (3)	1378·2 (*m*)	1379
1402 (0)				
1434 (0)		1444 (1*b*)	1445·2 (*f*)	
1455 (0)				1457
1499 (0)				1492
1588 (2)	1585·5 (2)	1580 (1)	1585·1 (*m*)	1550
1606 (3)	1604·7 (3)	1603 (5*b*)	1604·5 (*F*)	1613
1630 (0)	1628·5 (00)			
				1724
				1814
				1869
				1961
				2500
			2574·5 (*ff*)	
			2583·3 (*ff*)	
			2602·4 (*ff*)	
			2610·7 (*ff*)	
		2731 ($\frac{1}{2}$)		
2868 (3*vb*)	2865·8 (0)	2867 (3*b*)	2855·5 (*f*)	
			2874·6 (*f*)	

TABLE VIII—(*Contd.*)

Author	Howlett	Kohlrausch	Mesnage	Infra-red Absorption maxima
2922 (6*b*)	2919·9 (4)	2917 (10*b*)	2920·0 (*F*)	
			2978·9 (*f*)	
3002 ($\frac{1}{2}$)	3004·4 (0)		3000·3 (*f*)	2994
3037 (4*b*)	3035·4 (3)	3026 (4*b*)		
3058 (8)	3052·1 (5)	3055 (10*vb*)	3056·6 (*m*)	
3070 (6*b*)	3062·5 (4)		3059·0 (0)	
	3205·9 (0)			
				4150
				4586
				5848

TABLE IX. *Phenol.*

Author	Kohlrausch and Pongratz
243 (5*b*)	238 (7*b*)
507 ($\frac{1}{2}$)	504 ($\frac{1}{2}$)
532 (4)	530 (6)
590 (0)	
620 (4)	616 (5)
655 (00*d*)	
756 (3)	751 (3)
787 (0*b*)	
812 (8)	810 (10*b*)
830 (3)	826 (3)
	882 (00)
991 (00)	
1001 (10)	998 (12)
1013 (0)	
1027 (8*s*)	1025 (7)
1072 (1)	1068 (0)
(1113) (0)	
1155 (3*s*) }	1162 (5*b*)
1170 (4*s*) }	
1253 (2*b*)	1253 (4*b*)
(1425) (00)	
1464 (0)	
1498 ($\frac{1}{2}$)	
1595 (5) }	1599 (7*b*)
1605 (5) }	
3017 ($\frac{1}{2}b$)	
3051 (5) }	
3064 (8) }	3060 (12*b*)
3085 ($\frac{1}{2}$) }	
(3150) (00*d*)	
3200 (0*bd*)	
3524 (0*vb*)	3518 (0*vb*)

TABLE X.

Chlorobenzene.

Author	Murray and Andrews	Infra-red Absorption maxima
196 (6*b*)	198 (7)	
(270) ($\frac{1}{2}$)	275 (0)	
295 (2)	299 (2)	
420 (6)	419 (6)	
	465 (1)	
615 (3)	614 (3)	
702 (6)	703 (5)	
742 (0)	743 (1)	756
790 (0)		
830 (0)	832 (2)	820
		900
(925) (0)		
		943
989 (0*s*)		
1003 (10*s*)	1004 (10)	
1013 (00)		1014
1024 (7)	1023 (7)	
1084 (5)	1084 (5)	1071
1121 ($\frac{1}{2}$)	1122 (2)	1111
1158 ($\frac{1}{2}$)	1159 (3)	1149
1176 ($\frac{1}{2}$)	1174 (2)	
(1295)(0)		1250
1321 (0)	1324 (0)	1333
1372 (0)	1366 (0)	
	1402 (0)	
1443 (0)	1438 (1)	1441
	1475 (1)	1477
1565 (0)	1561 (1)	
1584 (4)	1584 (6)	1595
	2329 (0)	2326
3008 (0)	3005 (0)	
3028 (0)	3027 (0)	
3068 (10*b*)	3069 (10)	3068
3140 (0)	3141 (0)	
3165 (1)	3166 (0)	

TABLE XI. *Pyridine.*

Author	Krishnamurti	Kohlrausch and Pongratz	Infra-red Absorption maxima
(377) (0)	371 (0)		
402 (1)	403·6 (1)	401 (3)	
(553) (0)	?553 (0)		
602 (1)	603 (1½)	604 (4)	
652 (3)	651·9 (3)	652 (6)	
	717 (0)		
	747 (0)		752
799 (0)	806 (0)		806·5
			840·5
			855
878 (½)	885 (1)	880 (3)	888·6
			922
942 (0)	942 (0)		950
979 (0)			
990 (10)	992 (10)	990 (15)	992·6
1028 (10)	1029·4 (10)	1028 (12)	1028
1040 (0)			
1057 (0)	1067 (1)	1066 (0)	1069
1143 (½)	1145 (1)	1144 (2)	1139
1218 (3)	1218 (3)	1207 (7)	1211
			1290
			1370
(1444) (0)	1439 (0)		1439
1485 (1)	1483 (1½)	1479 (½)	1481
1570 (2)	1571·4 (4)		
1579 (2)	1580·8 (2)	1575 (6*b*)	
1594 (1)	1596·7 (1)		1600
			1724
			1923
2370 (0)	2368 (½)		
2449 (0)	2455 (½)		
(2658) (0)	2651 (0)		
2871 (0)	2867 (½)		
2908 (0)	2913 (½)		
2951 (1)	2952·2 (1)	2952 (1)	
2986 (0)	2985 (½)		
3025 (½)	3024 (1)		
3034 (½)			
3054 (8*b*)	3054 (10)	3053 (10*b*)	3077
3063 (½)			
3090 (½)	3089 (½)		
3142 (1½)	3144·1 (1½)		
3172 (½)	3175 (½)		
			3390
			5848
			5883

TABLE XII.
Cyclohexane.

Author	Krishnamurti	Infra-red Absorption maxima
384 ($\frac{1}{2}$)	381 ($\frac{1}{2}$)	
426 (1)	425 (1)	
(600) (0)		
	695 (0)	
802 (10)	802 (10)	840
(992) (0)	(992) (0)	909
1029 (6)	1028 (8)	1042
1156 (3)	1156 (1)	
1265 (5)	1266 (5)	1220
1348 (1)	1344 ($\frac{1}{2}$)	1323
1442 (5*b*)	1444 (5)	1435
2353 (0)	2351 (0)	
2467 (0)	2462 (0)	
2605 (0)		
2630 (1)	2630 (0)	
2662 (2)	2662 (1)	
2698 (1)	2695 ($\frac{1}{2}$)	
2853 (10*b*)	2852 (8)	2860
2870 (1)		
2888 (2)	2889 (1)	
2898 (2)		
2922 (8)	2922 (8)	
2937 (8)	2938 (8)	2940

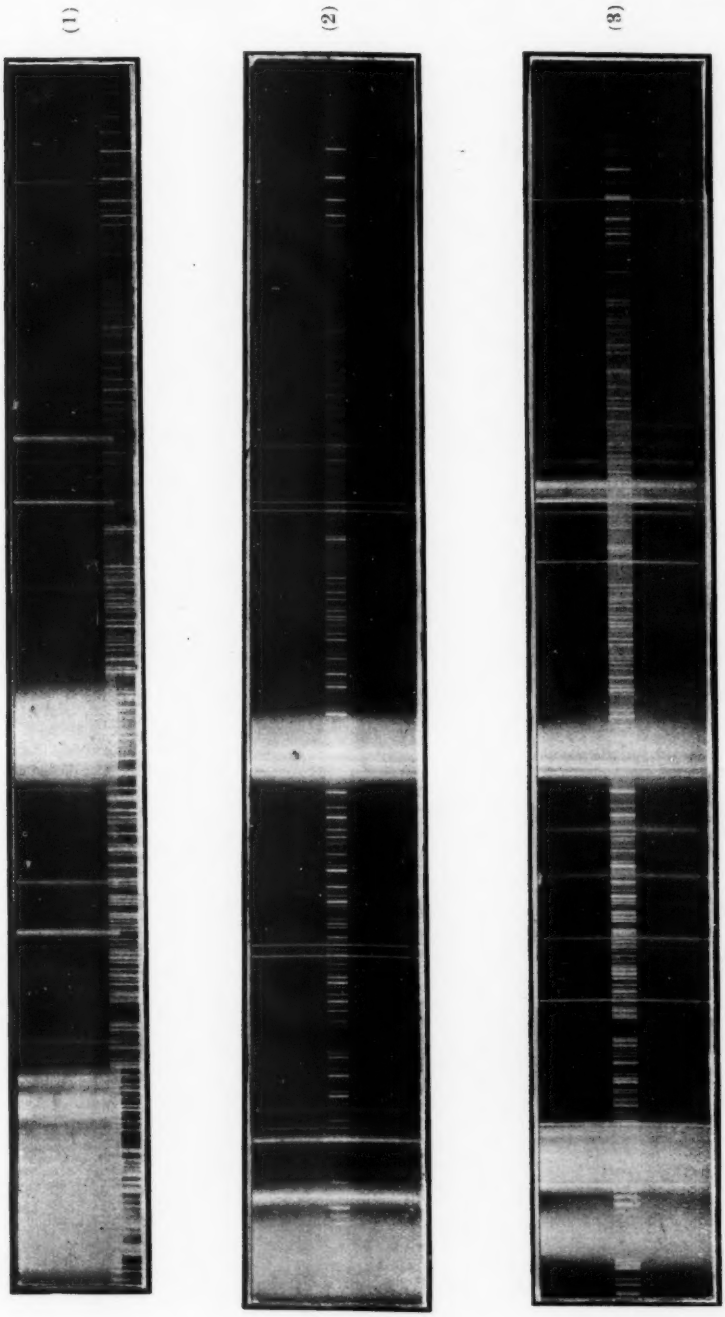

FIG. 1. Raman Spectra.
(1) Benzene; (2) Pyridine; (3) Cyclohexane.

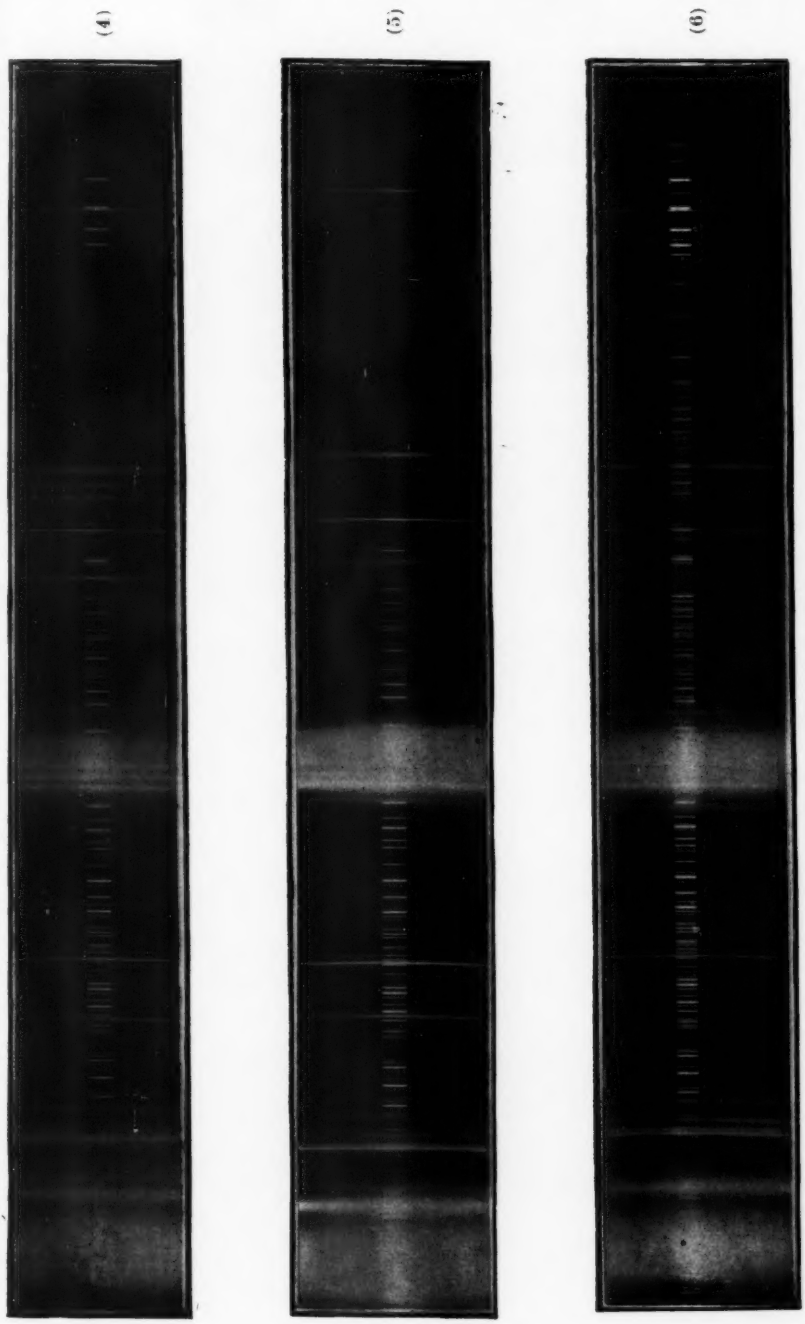

Fig. 2. Raman Spectra.
(4) Toluene, (5) Phenol, (6) Chlorobenzene.

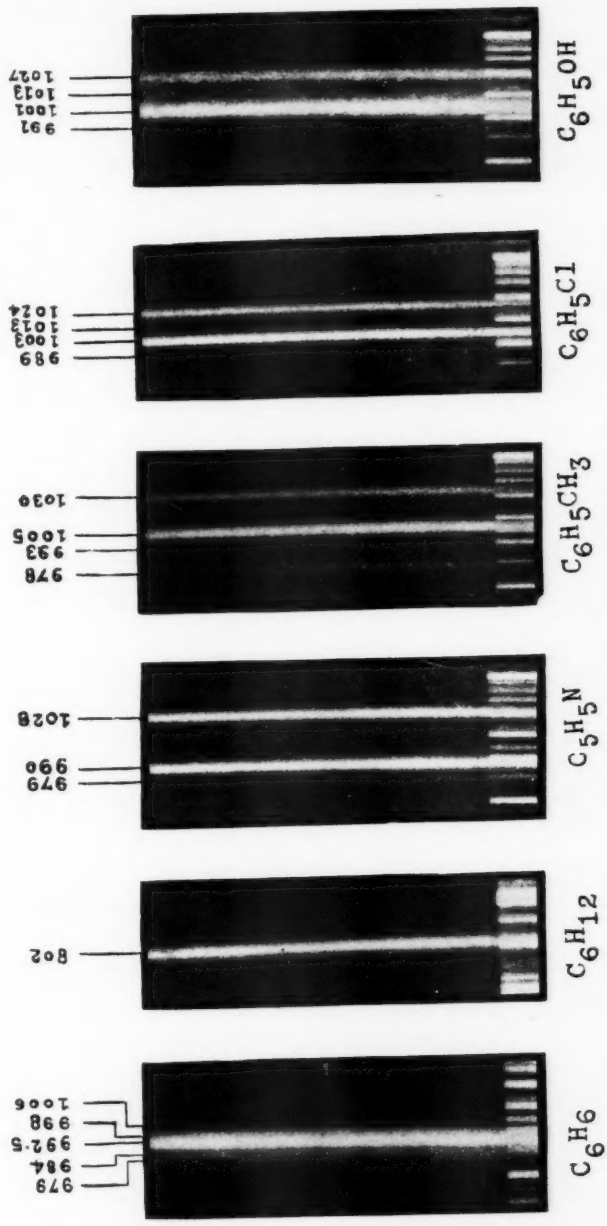

FIG. 3. Fine Structure of Raman Lines.

THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES : PART III.

Doppler Effect and Coherence Phenomena.

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1. Introduction.

In Part I[1] of this series of papers, a theory of the diffraction of light by high frequency sound waves was developed starting from the simple basic idea that the incident plane waves of light, after transmission through the medium traversed by the sound waves assume a corrugated form, owing to the fluctuations in the density and consequently also in the refractive index of the medium. The Fourier analysis of the emerging corrugated wave-front automatically gives the diffraction effects observed when the emergent waves are brought to focus by the lens of the observing telescope. The results deduced from the theory gave a gratifyingly satisfactory explanation of the observations of Bär[3] regarding the changes in the diffraction pattern when the supersonic intensity, the wave-length of the incident light and the length of the cell are varied.

In Part II[2], we extended the theory to the case of the oblique incidence of the light on the sound waves and were successful in explaining the variations of the diffraction effects reported by Debye and Sears[4] as the angle of obliquity is varied.

In Parts I and II, we deliberately ignored the variation of the refractive index with time in order to bring out the essential features of the theory without unnecessary complications. In this the third part of the paper, we proceed to take this factor also into consideration. It will be shown that light diffracted by progressive sound waves exhibits Doppler shifts of a very simple type. In the case, however, of the diffraction of light by *standing sound waves* in a medium, we get the much more interesting result that *in any even order, radiations with frequencies* $\nu \pm 2r\nu^*$ *would be present* where ν is the frequency of the incident light, ν^* is the frequency of sound in the

medium and r is any integer and that *in an odd order, radiations with frequencies* $\nu \pm \overline{2r+1}\,\nu^*$ *would be present.* This implies that *any pair of even orders or odd orders can partly cohere* and that *an even order and an odd one are incoherent.* This latter result has already been arrived at by Bär[5] purely by his experimental investigations. The remarkable results of Bär in the field of supersonic research thus find a natural explanation in terms of our theory.

It should be, however, noted that the theory developed in the following is subject to the same limitations as those in the previous parts, *viz.*, that the depth of the cell is not too great to permit the form of the emerging wave-front to be deduced in the simple manner indicated in Part I. A more general consideration of the problem will be presented in a later communication.

2. Doppler effects due to a progressive sound wave.

Let us suppose that the progressive sound wave travels in a direction parallel to the X-axis perpendicular to two faces of a rectangular vessel containing some homogeneous and isotropic medium. We use the same notation and the axes of reference as in our earlier paper. When the sound wave travels in the medium, the density of the medium and its refractive index undergo periodic fluctuations. If the sound wave is a simple one, we could assume that the variation of the refractive index at a point in the medium is given by

$$\mu(x, t) - \mu_0 = \mu \sin 2\pi(\nu^* t - x/\lambda^*) \qquad .. \qquad .. \quad (1)$$

where $\mu(x, t)$ is the refractive index of the medium at a height x from the origin at time t, μ_0 is the refractive index of the medium in its undisturbed state, μ is the *maximum variation* of the refractive index from μ_0 and ν^* and λ^* refer to the frequency and the wave-length of the sound wave in the medium.

Let the light wave be incident along the Z-axis perpendicular to two faces of the medium and the direction of the propagation of the sound wave. If the incident light wave is given by

$$\exp [2\pi i \nu t]$$

it will be

$$\exp [2\pi i \nu \{t - L\mu(x, t)/c\}]$$

when it arrives at the other face where L is the distance between the two faces.

The amplitude of the corrugated wave at a point on a distant screen parallel to the face of the medium from which light is emerging, whose join

with the origin has its x-direction-cosine l depends on the evaluation of the diffraction integral

$$\int_{-p/2}^{p/2} \exp\left[2\pi i \left\{lx - \mu L_1 \sin 2\pi\left(\nu^* t - x/\lambda^*\right)\right\}/\lambda\right] dx \qquad \ldots \qquad (2)$$

where p is the length of the beam along the X-axis. The real and the imaginary parts of the diffraction integral (2) are

$$\int_{-p/2}^{p/2} \left\{\cos ulx \cos\left(v \sin \overline{bx - \epsilon}\right) - \sin ulx \sin\left(v \sin \overline{bx - \epsilon}\right)\right\} dx \qquad \ldots \qquad (3)$$

and

$$\int_{-p/2}^{p/2} \left\{\sin ulx \cos\left(v \sin \overline{bx - \epsilon}\right) + \cos ulx \sin\left(v \sin \overline{bx - \epsilon}\right)\right\} dx$$

where $u = 2\pi/\lambda$, $b = 2\pi/\lambda^*$, $v = 2\pi\mu L_1/\lambda$ and $\epsilon = 2\pi\nu^* t$.

Putting $bx - \epsilon$ as x' we could write the integrals* (3) as

$$\frac{2}{b}\sum_0^{\infty\prime} J_{2r}(v) \int_{-bp/2-\epsilon}^{bp/2-\epsilon} \cos\left(ul\frac{x'+\epsilon}{b}\right) \cos 2rx'\, dx' - \frac{2}{b}\sum_0^{\infty} J_{2r+1}(v) \int_{-bp/2-\epsilon}^{bp/2-\epsilon} \sin\left(ul\frac{x'+\epsilon}{b}\right) \times \sin \overline{2r+1}\, x'\, dx'$$

and

$$\frac{2}{b}\sum_0^{\infty\prime} J_{2r}(v) \int_{-bp/2-\epsilon}^{bp/2-\epsilon} \sin\left(ul\frac{x'+\epsilon}{b}\right) \cos 2rx'\, dx' + \frac{2}{b}\sum_0^{\infty} J_{2r+1}(v) \int_{-bp/2-\epsilon}^{bp/2-\epsilon} \cos\left(ul\frac{x'+\epsilon}{b}\right) \times \sin \overline{2r+1}\, x'\, dx'$$

or

$$\frac{1}{b}\sum_0^{\infty\prime} J_{2r}(v) \int_{-bp/2-\epsilon}^{bp/2-\epsilon} \left\{\cos\left(\overline{\frac{ul}{b} + 2r}\, x' + \frac{ul\epsilon}{b}\right) + \cos\left(\overline{\frac{ul}{b} - 2r}\, x' + \frac{ul\epsilon}{b}\right)\right\} dx'$$

$$+ \frac{1}{b}\sum_0^{\infty} J_{2r+1}(v) \int_{-bp/2-\epsilon}^{bp/2-\epsilon} \left\{\cos\left(\overline{\frac{ul}{b} + \overline{2r+1}}\, x' + \frac{ul\epsilon}{b}\right) - \cos\left(\overline{\frac{ul}{b} - \overline{2r+1}}\, x' + \frac{ul\epsilon}{b}\right)\right\} dx' \qquad \ldots \qquad (4a)$$

---

* The dash over the summation sign indicates that the co-efficient of the first term has to be multiplied by half,

and

$$\frac{1}{b}\sum_0^{\infty}{}' J_{2r}(v)\int_{-bp/2-\epsilon}^{bp/2-\epsilon}\left\{\sin\left(\frac{ul}{b}+2r\,x'+\frac{ul\epsilon}{b}\right)+\sin\left(\frac{ul}{b}-2r\,x'+\frac{ul\epsilon}{b}\right)\right\}dx'$$

$$+\frac{1}{b}\sum_0^{\infty} J_{2r+1}(v)\int_{-bp/2-\epsilon}^{bp/2-\epsilon}\left\{\sin\left(\frac{ul}{b}+\overline{2r+1}\,x'+\frac{ul\epsilon}{b}\right)-\sin\left(\frac{ul}{b}-\overline{2r+1}\,x'+\frac{ul\epsilon}{b}\right)\right\}dx' \quad .. \quad (4b)$$

Integrating and combining the real and the imaginary parts (4*a*) and (4*b*) we find that the amplitude depends on

$$p\sum_0^{\infty}{}' J_{2r}(v)\left\{\frac{\sin\{(ul+2rb)p/2\}}{(ul+2rb)p/2}e^{-i2r\epsilon}+\frac{\sin\{(ul-2rb)p/2\}}{(ul-2rb)p/2}e^{i2r\epsilon}\right\}$$

$$+p\sum_0^{\infty} J_{2r+1}(v)\left\{\frac{\sin\{(ul+\overline{2r+1}\,b)p/2\}}{(ul+\overline{2r+1}\,b)p/2}e^{-i\overline{2r+1}\epsilon}-\frac{\sin\{(ul-\overline{2r+1}\,b)p/2\}}{(ul-\overline{2r+1}\,b)p/2}e^{i\overline{2r+1}\epsilon}\right. \quad .. \quad (5)$$

where $\epsilon = 2\pi\nu^* t$. We should remember that the amplitude function has the other time factor $e^{2\pi i\nu t}$ which has been taken out as a constant from the integrand of the diffraction integral. One can see that the magnitude of each individual term of (5) attains its highest maximum when its denominator vanishes. Also, it can be seen that when any one of the terms is maximum, all the others have negligible values as the numerator of each cannot exceed unity and the denominator is some integral non-vanishing multiple of b which is sufficiently large. When

$$ul + nb = 0$$

$$\sin\theta = -\frac{n\lambda}{\lambda^*} \quad .. \quad .. \quad .. \quad .. \quad (6)$$

where n is a positive or a negative integer and θ is the angle between the direction whose x-direction-cosine is l and the Z-axis.

The wave travelling in the direction whose inclination with the incident light beam is $\sin^{-1}(-n\lambda/\lambda^*)$ is determined by

$$J_n(v)e^{2\pi i(\nu - n\nu^*)t} \quad .. \quad .. \quad .. \quad .. \quad (7)$$

having the frequency $\nu - n\nu^*$, n being a positive or negative integer; when n is negative the direction of propagation of that order has positive direction-cosines with respect to the directions of the propagation of the sound and light waves. Consequently the radiations in the different orders will be incoherent with each other. (See Fig. 1.)

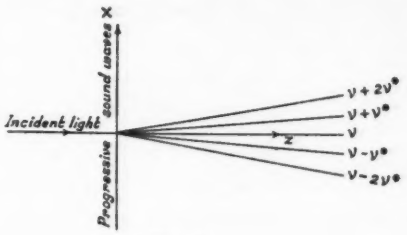

FIG. 1.

The relative intensity of the mth order to the nth order is given by the expression

$$J_m^2\left(\frac{2\pi\mu L_1}{\lambda}\right)\Big/J_n^2\left(\frac{2\pi\mu L_1}{\lambda}\right)$$

identical with the one given in Part I.

3. Doppler effects due to a standing sound wave.

In the case of a standing wave produced by the interference of two simple waves travelling in opposite directions parallel to the X-axis, we could assume that the variation of the refractive index at a point in the medium is given by

$$\mu(x, t) - \mu_0 = -\mu \sin 2\pi\nu^* t \sin (2\pi x/\lambda^*) \quad .. \quad .. \quad (8)$$

with the same notation as in the previous section. Under the same restrictions as in Part I, we find that the emerging wave-front is given by

$$\exp [2\pi i\nu \{t - L_1\mu (x, t)/c\}] \quad .. \quad .. \quad .. \quad .. \quad (9)$$

The diffraction integral is then

$$\int_{-p/2}^{p/2} \exp [2\pi i \{lx + \mu L_1 \sin \epsilon \sin (2\pi x/\lambda^*)\}/\lambda]\, dx \quad .. \quad .. \quad (10)$$

where $\epsilon = 2\pi\nu^* t$.

The real and the imaginary parts of the integral (10) are

$$\int_{-p/2}^{p/2} \{\cos ulx \cos (v' \sin bx) - \sin ulx \sin (v' \sin bx)\}\, dx$$

and

$$\int_{-p/2}^{p/2} \{\sin ulx \cos (v' \sin bx) + \cos ulx \sin (v' \sin bx)\}\, dx$$

where

$$u = 2\pi/\lambda,\ b = 2\pi/\lambda^*,\ v' = v \sin \epsilon = (2\pi\mu L_1 \sin \epsilon)/\lambda$$

Following the same procedure as in our earlier paper, we find that the real part of the diffraction integral (10) is

$$p \sum_0^{\infty\prime} J_{2r}\,(v \sin 2\pi\nu^* t) \left\{\frac{\sin\,[(ul+2rb)p/2]}{(ul+2rb)p/2} + \frac{\sin\,[(ul-2rb)p/2]}{(ul-2rb)p/2}\right\}$$

$$+ p \sum_0^{\infty} J_{2r+1}(v \sin 2\pi\nu^* t) \left\{\frac{\sin\,[(ul+\overline{2r+1}\,b)p/2]}{(ul+\overline{2r+1}\,b)p/2} - \frac{\sin\,[(ul-\overline{2r+1}\,b)p/2]}{(ul-\overline{2r+1}\,b)p/2}\right\}.$$

The integral corresponding to the imaginary part of the diffraction integral is zero.

Following similar arguments as in Part I or in the previous section we can show that the wave travelling in the direction given by

$$ul + nb = 0$$

or

$$\sin\theta = -\frac{n\lambda}{\lambda^*}$$

is

$$\pm J_n\,(v \sin 2\pi\nu^* t)\, e^{2\pi i\nu t} \quad .. \quad .. \quad .. \quad (11)$$

multiplied by a constant usually taken out from the diffraction integral. The wave given by (11) is not a simple one but is a superposition of a number of waves given by the Fourier analysis of $J_n(v \sin 2\pi\nu^* t)$ and multiplied by $e^{2\pi i\nu t}$.

Fourier Analysis of $J_n\,(v \sin\epsilon)$: The well-known Neumann's addition theorem

$$J_0(\tilde{\omega}) = 2 \sum_0^{\infty\prime} J_m(Z)\; J_m(z) \cos m\phi$$

where

$$\tilde{\omega} = \sqrt{(Z^2 + z^2 - 2Zz \cos\phi)}$$

has been generalised by Graf[6] as

$$J_n(\tilde{\omega}) \left\{\frac{Z - ze^{-i\phi}}{Z - ze^{i\phi}}\right\}^{n/2} = \sum_{-\infty}^{+\infty} J_{n+m}(Z) J_m(z) e^{im\phi}$$

provided $|ze^{\pm i\phi}| < Z$. If n is an integer, the inequality need not be in force. Putting

$$Z = z = v/2$$

and $$\phi = 2\epsilon$$

we get

$$J_n\,(v \sin\epsilon) e^{-in\epsilon}(-1)^{n/2} = \sum_{-\infty}^{+\infty} J_{n+m}(v/2) J_m(v/2) e^{i2m\epsilon}.$$

From this, changing n to $2n$ we deduce that

$$J_{2n}(v \sin\epsilon) = (-1)^n \sum_{-\infty}^{+\infty} J_{m+2n}(v/2)\; J_m(v/2) e^{-i(2m+2n)\epsilon}.$$

Putting $m = -n + r$ and after a little simplification, we get

$$J_{2n}(v \sin \epsilon) = (-1)^n J_{-n}(v/2)J_n(v/2) + 2 \sum_1^\infty J_{-n+r}(v/2)J_{n+r}(v/2) \cos 2r\epsilon$$

$$= (-1)^n 2 \sum_0^\infty{}' J_{-n+r}(v/2)\, J_{n+r}(v/2) \cos 2r\epsilon$$

$$= 2 \sum_0^\infty{}' (-1)^r J_{n-r}(v/2)\, J_{n+r}(v/2) \cos 2r\epsilon.$$

Similarly we can deduce that

$$J_{2n+1}(v \sin \epsilon) = 2 \sum_0^\infty (-1)^r J_{n-r}(v/2)\, J_{n+r+1}(v/2) \sin 2r+1\epsilon$$

$$J_{2n}(v \cos \epsilon) = 2 \sum_0^\infty{}' J_{n-r}(v/2)\, J_{n+r}(v/2) \cos 2r\epsilon$$

$$J_{2n+1}(v \cos \epsilon) = 2 \sum_0^\infty J_{n-r}(v/2)\, J_{n+r+1}(v/2) \cos \overline{2r+1}\epsilon.$$

Returning now to the Fourier analysis of the diffraction components, the diffracted waves can be resolved into a number of simple waves, for

$$J_{2n}(v \sin 2\pi\nu^* t)\, e^{2\pi i\nu t}$$

$$= e^{2\pi i\nu t}\, 2 \sum_0^\infty{}' (-1)^r J_{n-r}(v/2)J_{n+r}(v/2) \cos (2r \cdot 2\pi\nu^* t)$$

$$= \sum_0^\infty{}' (-1)^r J_{n-r}(v/2)J_{n+r}(v/2) \{e^{2\pi i(\nu+2r\nu^*)t} + e^{2\pi i(\nu-2r\nu^*)t}\}$$

and

$$J_{2n+1}(v \sin 2\pi\nu^* t)\, e^{2\pi i\nu t}$$

$$= \frac{1}{i} \sum_0^\infty (-1)^r J_{n-r}(v/2)J_{n+r+1}(v/2) \{e^{2\pi i(\nu+2\overline{r+1}\ \nu^*)t} - e^{2\pi i(\nu-2\overline{r+1}\ \nu^*)t}\}$$

Thus in all even orders radiation frequencies

$$\nu \pm 2r\,\nu^*, \quad r \text{ a positive integer},$$

are present. The relative intensity of the $\nu \pm 2r\nu^*$ sub-component in the $2n$th order is given by

$$J_{n-r}^2\,(v/2)\, J_{n+r}^2(v/2).$$

In all odd orders radiation frequencies

$$\nu \pm \overline{2r+1}\ \nu^*, \quad r \text{ a positive integer},$$

are present. (See Fig. 2.) The relative intensity of the $\nu \pm \overline{2r+1}\ \nu^*$ sub-component in $2n+1$th order is given by

$$J_{n-r}^2\,(v/2)\, J_{n+r+1}^2\,(v/2).$$

We can conclude from the above analysis that *an even order and an odd one are incoherent while any two even or any two odd orders can partly cohere.* Any two orders symmetrically situated to the 0th order are completely coherent.

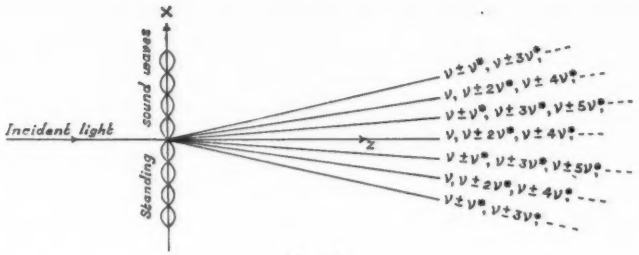

FIG. 2.

We have calculated the relative intensities of the various Doppler sub-components of the various orders as v ranges from 0 to 5 in steps of unity and represented them in Fig. 3.

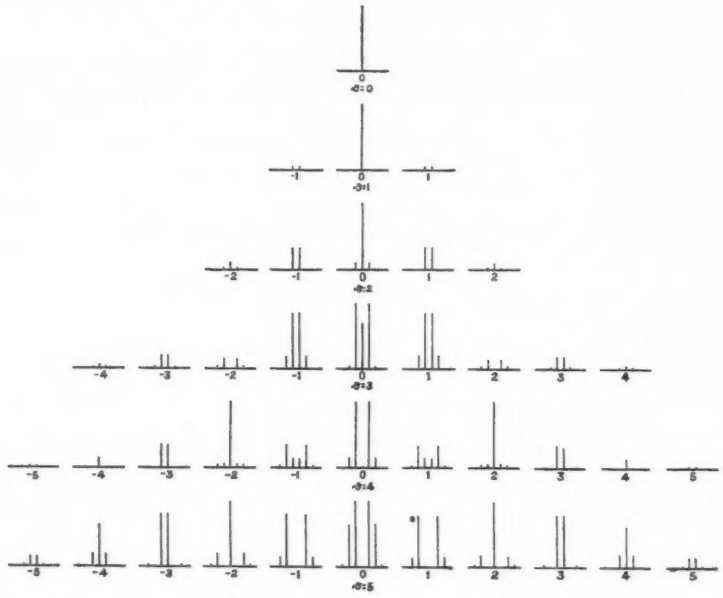

FIG. 3.

Relative intensities of the various sub-components of observable orders; the sub-components of an odd order standing on a base correspond to $- - -$, $\nu - \overline{2r+1}\,\nu^*, - - -, \nu - \nu^*, \nu + \nu^*, - - -$, $\nu + \overline{2r+1}\,\nu^*, - - -$ and those of an even order standing on a base correspond to $- - -, \nu - 2r\,\nu^*, - - -, \nu, -\ -, \nu + 2r\nu^*, - - -$. In the figure $v = 5$, some lower orders are missing as their relative intensities are negligibly small.

We may also note that the intensity of each of the sub-components of each order depends on the amplitude of the supersonic vibration, the length of the cell and the wave-length of the incident light.

If we ignore the spectral character of each order, then the relative intensity of the mth order to the nth order is

$$\frac{\int_0^{2\pi} J_m^2 (v \sin\theta)\, d\theta}{\int_0^{2\pi} J_n^2 (v \sin\theta)\, d\theta} \quad \text{where } v = \frac{2\pi\mu I_c}{\lambda}$$

which follows from Parseval's Theorem.

4. Interpretation of Bär's experimental results.

Bär[5] has recently investigated by an interference method the coherence of the diffraction components of light produced by a standing supersonic wave. He has found that the various orders could be classed into two groups, one comprising the even orders and the other comprising the odd orders and that any two orders of a group cohere partly while two orders from different groups are completely incoherent. These results are readily understood when we notice that an even order contains radiations with frequencies $\nu \pm 2r\nu^*$ while an odd order contains radiations with frequencies $\nu \pm (2r+1)\nu^*$. The experimental results of Bär are thus fully explicable in terms of the theory we have developed in the previous section. Bär has himself remarked that the observed coherence indicates the presence of a series of frequency components in each of the diffraction spectra. It will be noticed that, according to our theory, even the zero-order spectrum includes such a series of frequency components.

5. Summary.

The theory developed in Part I of this series of papers has been developed in this paper to find the Doppler effects in the diffraction components of light produced by the passage of light through a medium containing (1) a progressive supersonic wave and (2) a standing supersonic wave.

(1) In the case of the former the theory shows that the nth order which is inclined at an angle $\sin^{-1}\left(-\frac{n\lambda}{\lambda^*}\right)$ to the direction of the propagation of the incident light has the frequency $\nu - n\nu^*$ where ν is the frequency of light, ν^* is the frequency of sound and n is a positive or negative integer and that the nth order has the relative intensity $J_n^2\left(\frac{2\pi\mu I_c}{\lambda}\right)$ where μ is the maximum variation of the refractive index, I_c is the distance between the faces of the cell of incidence and emergence and λ is the wave-length of light.

(2) In the case of a standing supersonic wave, the diffraction orders could be classed into two groups, one containing the even orders and the other odd orders; any even order, say $2n$, contains radiations with frequencies $\nu \pm 2r\nu^*$ where r is an integer including zero, the relative intensity of the $\nu \pm 2r\nu^*$ sub-component being $J^2_{n-r}\left(\frac{\pi\mu L_z}{\lambda}\right) J^2_{n+r}\left(\frac{\pi\mu L_z}{\lambda}\right)$; any odd order, say $2n+1$, contains radiations with frequencies $\nu \pm \overline{2r+1}\nu^*$, the relative intensity of the $\nu \pm \overline{2r+1}\nu^*$ sub-component being $J^2_{n-r}\left(\frac{\pi\mu L_z}{\lambda}\right) J^2_{n+r+1}\left(\frac{\pi\mu L_z}{\lambda}\right)$. These results satisfactorily interpret the recent results of Bär that any two odd orders or even ones partly cohere while an odd one and an even one are incoherent.

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